SUDBURY ENVIRONMENTAL STUDY

STUDIES OF LAKES AND WATERSHEDS NEAR SUDBURY ONTARIO: FINAL LIMNOLOGICAL REPORT.

SES 009/82

by

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MAJOR CONCLUSIONS

1. The exceptionally high input of Cu, Ni, Zn, Fe, Mn, and Al to the study lakes is a result of activities of the local smelting industry. Evaluation of historical metal inputs through examination of lake sediment chronologies showed that elevated inputs were contemporaneous with the opening of the Falconbridge and Copper Cliff smelters at Sudbury (50 ± 10 yr before present). Almost all of the Cu, Ni, Zn and some of the Fe inputs to the lakes result from direct atmospheric deposition. When the Inco Ltd. smelters were not operating, between September, 1978 and April, 1979, bulk deposition of Cu and Ni was reduced by almost two orders of magnitude to background levels measured in Ontario locations with no local sources of metals.

   The atmospheric deposition of strong acid has increased the output of Al, Mn and Fe from the watersheds to the lakes. In order to reduce lake concentrations of metals to those specified as acceptable by the Great Lakes Water Quality Objectives, inputs of Cu and Ni must be reduced by at least 90%, and inputs of Fe and Zn by 50 to 60%. A 70% reduction in watershed output of Al is required to decreased lake concentrations of Al to 100 μgL^{-1}. Such a reduction in Al outputs can only be achieved by a large reduction in the deposition of strong acid.

2. Mass balances for the calibrated lakes and watersheds demonstrated that 50% (at 30 km distance from Copper Cliff) to 85% (at 4 km distance) of the total deposition of strong acid was not measured by bulk collectors. The unmeasured

input of acid was shown to be the result of dry deposition of sulphur dioxide which must have been largely of local origin. While deposition of strong acid measured using bulk collectors was not reduced during the shutdown of the Inco Ltd. smelters, the total deposition of strong acid must, therefore, have been substantially reduced.

3. Treatment of acidic lakes with $CaCO_3/Ca(OH)_2$ raised the pH and in most cases supplied residual acid neutralizing capacity (ANC) for extended periods of time. The duration of effective treatment depended on the rate of supply of strong acid to the lakes and on their hydrologic budgets. One of the four treated lakes re-acidified within two years of the final addition of base. The rate of loss of ANC, i.e. the acidification rate, could be estimated from consideration of an alkalinity mass balance. Considerable ANC was apparently provided by biological processes in the lakes, especially nitrate reduction, and by the lake sediments. Concentrations of trace metals, especially Cu, remained sufficiently high after neutralization that fish failed to survive when introduced to the lakes.

SUMMARY

Chapter 1: Characterization of Lakes near Sudbury, Ontario

1. From 1973 to 1979, Clearwater Lake, near Sudbury, Ontario, was intensively monitored as a reference for manipulation experiments performed on 6 other Sudbury area lakes (Middle, Hannah, Lohi, Nelson, Mountaintop and Labelle Lakes), and to provide information on long-term variability of the chemistry and biota of an acidic lake. Clearwater, Lohi, Middle, Hannah and Mountaintop Lakes were all acidic lakes ($pH < 4.6$) with no fish populations, prior to manipulations. Labelle and Nelson Lakes were much less acidic ($pH = 6.0$ and 5.8, respectively) and supported fisheries.
2. Average concentrations of Cu, Ni, Zn, Al and Mn in Clearwater Lake in 1977 were 81, 280, 39, 380 and 290 $\mu g\ L^{-1}$, respectively. Trace metal concentrations decreased in the 6 other lakes at increasing distance from Sudbury, but even at Mountaintop Lake, 50 km from the city, levels of Zn, Cu and Ni were well above background levels and levels in south-central Ontario lakes that are near no industrial centres, but are receiving acidic precipitation.
3. Levels of major cations were much higher in Clearwater Lake than in south-central Ontario lakes, and decreased in lakes at increasing distance from Sudbury. Replacement of HCO_3^- by SO_4^{2-} as the dominant anion in Clearwater Lake indicated that acidification of the lake was probably attributable to the deposition of acidic sulphates.

4. Clearwater Lake was exceptionally clear. In consequence, the lake had a much thicker epilimnion, a warmer hypolimnion, and fall overturn occurred 4 to 8 weeks earlier than in a non-acidic, oligotrophic lake of similar morphometry and fetch. As the entire lake was included in the trophogenic zone, depression of NO_3^- levels to below detection limits in the hypolimnion was probably attributable to photosynthetic activity in the profundal waters.
5. Biomass and productivity of the phytoplankton community of Clearwater Lake were not reduced by the low pH. Phytoplankton community diversity, estimated by richness of genera, was reduced and community structure was altered. Dinoflagellates, especially *Peridinium inconspicuum* replaced the chrysophytes or diatoms that typically are dominant in non-acidic lakes.
6. *Eriocaulon septangulare*, *Eleocharis acicularis* and *Myriophyllum tenellum* dominated the macrophyte communities. The communities were similar in structure (dominated by isoetids forms), but impoverished in species in comparison with 24 lakes in south-central Ontario. Macrophyte standing stock was much higher in Clearwater Lake than in 2 non-acidic, oligotrophic lakes in south-central Ontario; in fact, it was as high as that observed in eutrophic Chemung Lake in southern Ontario. Dense beds of *Sphagnum*, similar to those reported in acidic Scandanavian lakes, were not observed in Sudbury lakes.
7. Zooplankton communities were apparently influenced by both the lower pH and the high levels of metals in the acidic study lakes. Species richness was 3-4 times lower than in non-acidic lakes. *Bosmina longirostris* was the dominant crustacean zooplankter, forming 78-95% of the average crustacean biomass

in Clearwater Lake. In contrast with phytoplankton, zooplankton standing stocks were reduced, because of low densities and smaller size of the community dominants. Rotifers, especially _Keratella taurocephala_, were much more important components of the zooplankton in Clearwater Lake than in non-acidic lakes.

Chapter 2: Atmospheric deposition of major ions, nutrients and trace metals in the Sudbury area

1. Bulk deposition of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, TP, NO_3^-, NH_4^+, TKN, Fe, Mn, Al, Cu, Ni, Zn and Pb was measured for the period June 1977 to December 1979 for 3 stations in the Sudbury area; namely, Sudbury North (30-50 km north of Copper Cliff), Sudbury Center (4-5 km south), and Sudbury South (10-12 km south). Wet-only deposition was also measured at Sudbury North and Sudbury Center for May/June to October/November from 1977 to 1979.
2. The major cations in bulk deposition (on an equivalent basis) were $H^+ > Ca^{2+} \sim Na^+ \sim NH_4^+ > Mg^{2+} > K^+$. The major anions were in the order $SO_4^{2-} > NO_3^- > Cl^-$. The ions balanced within 17, 10 and 24% for 1978, and 15, 7 and 6% for 1979 for Sudbury North, Sudbury Center and Sudbury South, respectively. Cations were always in excess.
3. Deposition of materials in precipitation varied in time and in space. Deposition of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, TP, TKN and Zn was greatest during the summer when precipitation depth was greatest. Most of the annual Cu and Ni deposition occurred in the summer at Sudbury North, while Cu,

Ni and Zn deposition was greatest in the winter at Sudbury Centre and South. Spatial variation in the deposition of SO_4^{2-}, Cu, Ni, and Fe was related to smelter emissions. Deposition rates for these substances decreased with increasing distance from the smelters.

4. Deposition rates of Al, Mn, nutrients and major ions, excepting SO_4^{2-}, were similar or only slightly higher at the Sudbury stations than rates in south-central Ontario. However, deposition rates of Cu, Ni, Zn, Fe and SO_4^{2-} were strongly influenced by local smelting activities, in fact, Cu and Ni deposition rates exceeded virtually all previously reported values for industrialized areas. Even at Sudbury North, the station with the lowest trace metal deposition rates, levels were 4-, 4- and 20-fold higher than in south-central Ontario for Zn, Ni and Cu, respectively. During a period of time when smelters of Inco Ltd. were not operating, bulk deposition rates of these metals decreased to levels typical of south-central Ontario.

5. Wet deposition exceeded dry deposition for H^+, SO_4^{2-}, NO_3^-, NH_4^+ and Ni at Sudbury North and Center, while dry input exceeded wet for Na^+, Cl^-, TP, Fe, Cu and Zn. The dry component of the precipitation was generally more important than in south-central Ontario.

6. Deposition rates of gaseous SO_2 were estimated as the product of atmospheric SO_2 concentrations and a deposition velocity of 0.8 cm sec^{-1}. Gaseous inputs calculated as SO_4^{2-} were 50-70% of bulk deposition at Sudbury North and South and approximately equal at Sudbury Center. The SO_2 deposition rates decreased during the shutdown at Inco Ltd.

7. Sulphuric acid contributed approximately twice as much as nitric acid to the strong acidity of bulk deposition at Sudbury, and was even more important when gaseous SO_2 inputs were considered. Seasonal variations in rates of SO_4^{2-} deposition did occur, resulting in relatively greater nitric acid contributions to total acidity in the winter. Even in the winter, however, nitric acid contributed <50% of the total strong acid inputs.

Chapter 3: Sediment chemistry and rates of sedimentation in lakes near Sudbury, Ontario

1. The sedimentation rates of the hypolimnetic sediments of Lohi and Clearwater Lakes increased by 200-400% about 40-50 years BP (before present). Prior to these changes, the sedimentation rates were typical for oligotrophic Precambrian lakes (5-10 mg cm^{-2} yr^{-1}). In cores that had no mixing zone in the upper layers, the sedimentation rates declined to the early levels in approximately the last 2 decades.
2. The concentrations in and deposition rates to the sediments of Cu, Ni and Pb have increased by 1 to 2 orders of magnitude relative to background levels. Cd, Fe and Zn concentrations have also increased, but by lesser amounts (generally 100% to 1 order of magnitude). These increases coincide with a decrease in Al concentration which reflects acidification of the lake. The major changes in Cu, Ni, Cd, Fe, Zn, Pb and Al occurred simultaneously, about 50 ±15 yr BP. These changes coincided with the increased Ni and Cu production at Sudbury, with the Falconbridge Smelter opened in 1929 and the Copper Cliff tall

stack (155 m) opened in 1930.

3. The concentration of phosphorus in the sediments of Lohi and Clearwater Lakes decreased ~40-45 yr BP. A small increase in the uppermost layer (~1 cm) in Lohi Lake reflects the effect of the neutralization treatments. The accumulation rates of P increased greatly ~40-45 yr BP, because of the increase in sedimentation rates, then decreased to rates that were lower than those indicated as background rates (>45 yr BP).
4. The concentrations of Cu, Ni, Zn, Pb, Cd and Fe were greater in the upper or recent sediments (~1.5 g cm^{-2}) in Middle and Hannah Lakes than in deep or background sediments, by factors that were comparable to those measured for Clearwater and Lohi Lakes.
5. The organic content (LOI) and phosphorus and nitrogen concentrations of the sediments of Middle and Hannah Lakes decreased at about the same time as the metal concentrations increased. There was a rapid increase in concentration of these 3 parameters in the most recent sediments (~0.1 g cm^{-2}), which is attributable to the neutralization and fertilization treatments of the lakes.

Chapter 4: Components of the water balance of lakes near Sudbury, Ontario

1. Hydrological data were obtained for Hannah, Middle, Clearwater, Lohi and Nelson Lakes for the period June 1977 to December 1979. Each component of the annual water balance of the lakes was measured or estimated separately (precipitation, surface runoff, loss via outflow, evaporation, groundwater, and change

in lake storage). Balances to within 10% were achieved for the 1978 and 1979 calendar years, giving confidence in the use of the data for the construction of chemical mass balances.

2. From 11 to 40% of the annual water supply to the lakes was provided by precipitation directly to the lake's surface, the remainder provided by surface runoff. Surface runoff data showed that the 5 headwater basins had significantly different hydrological responses than the 5 lake outlets with respect to unit yield and peak flow/mean flow. The data also suggested that Nelson inlet 3 had different hydrological characteristics (unit yield, spring flow/annual flow, peak flow/mean flow, base flow/total flow) than the other headwater basins, because it had a greater amount of surficial material deposited in its basin.
3. From 65 to 91% of the annual water loss from the lakes was via the outlet, the remainder via evaporation. The monthly pattern of lake evaporation (as calculated by an energy balance) differed from lake to lake because of differing heat storage capacities.

Chapter 5: Stream Chemistry - Geochemical interactions of watersheds with precipitation near Sudbury, Ontario

1. The factors controlling stream chemistry and the export of materials from watersheds were examined in 11 headwater watersheds of Middle, Clearwater and Nelson Lakes. The mean concentrations of H^+, Ca^{2+}, Cl^-, NO_3^-, NH_4^+, Cu, Ni and Zn varied more than 10-fold between streams. With a few exceptions, temporal variation was generally small for major

ions (<10-fold) and large (>10-fold) for nutrients, Cu, Ni and Zn. All variations in concentration were small compared to variations in flow within a stream.

2. The dominance of SO_4^{2-} and absence of HCO_3^- in most streams suggested that mineral weathering in the Sudbury area is primarily driven by the input of strong acids, rather than by the dissociation of carbonic acid as occurs in watersheds not affected by anthropogenic activities. The order of cation dominance ($Ca^{2+} > Mg^{2+} > Na^+ > K^+$) in the streams is in general agreement with that expected for felsic geochemical environments.

3. Stepwise multi-linear regression was used to quantify relationships between physical and geological characteristics of the 11 watersheds and their associated stream chemistry. The presence of roadways and the types of surficial deposits in the watersheds were generally the most important characteristics explaining stream concentration.

4. Great variability in gross export was observed for the 19 chemical species analyzed and could largely be explained on the basis of geology or the existence of roadways in the watershed. On a mass basis, SO_4^{2-}, Ca^{2+} and Si were the dominant substances exported. In general, material export from Sudbury watersheds is at the high end of the ranges reported for Shield watersheds.

5. The watersheds generally exhibited positive values of net export (gross export-input) for Ca^{2+}, SO_4^{2-}, Mg^{2+}, Mn, K^+, Al, Ni, alkalinity and Si. Total P, NO_3^-, NH_4^+, TKN and H^+ were consistently retained within the watersheds, while Na^+, Cl^-, Cu, and Fe gave different results in different

years. These differences were attributable to the biogeochemical reactions of the substances in the watersheds, and/or to varying inputs of materials to the watersheds. Net export of ions at Sudbury was generally at the high end of the range reported elsewhere for watersheds underlain by silicate bedrock.

6. When net export for the 11 watersheds was examined on a monthly basis, different patterns were apparent for different substances. Only alkalinity was consistently lost from the watersheds in all months of the study, while in contrast, H^+, NO_3^-, NH_4^+ and TKN were retained in almost all watersheds at all times. All other chemical species exhibited "cross-patterns", eg. having net loss in spring and fall, and net retention in summer and sometimes winter.
7. The source of acid (natural or anthropogenic) driving weathering reactions in the 11 watersheds at Sudbury was assessed by considering the components of acid supply and consumption. Consistently more acid was consumed by the watersheds than was apparently supplied. The "missing" or unmeasured acid supply was inferred to be SO_2 deposited during dry periods, since, a) the atmospheric deposition of this parameter was known to be an underestimate (see Chapter 2), and b) the watersheds exhibited large net export of SO_4^{2-}, despite the fact that no readily apparent source of S was present within them. These results show that anthropogenically-supplied strong acids are the dominant driving force for weathering at Sudbury, and that the dry deposition of SO_2 is 1.2- to 2.6-fold greater than the sum of all other measured acid inputs.

Chapter 6: Experimental neutralization of lakes near Sudbury, Ontario

1. The pH of Middle, Lohi and Hannah Lakes was raised by additions of base from 4.3 - 4.4 to near neutrality. In Middle and Hannah Lakes, average pH remained >6.5 until the end of the study (1980), while in Lohi Lake, added acid neutralizing capacity (ANC) was exhausted in the spring of 1977. By 1979 the pH had decreased to 4.7. The pH of Lohi Lake decreased because: a) it received a higher volumetric supply of acid than did Middle and Hannah Lakes, b) concentrations of ANC remaining immediately after additions of base were much lower in Lohi Lake than in Middle and Hannah Lakes and c) fertilization of Middle and Hannah Lakes resulted in generation of more alkalinity than was generated by the biota in Lohi Lake.
2. In Middle, Lohi and Hannah Lakes, 30-41% of the added ANC was consumed by reaction with Al^{3+}, Cu^{2+} and Ni^{2+}, 1-3% by hydroxylation of trace metals other than Al, Cu and Ni, 5-20% by direct reaction with H^+, and, by residual, 31-44% by neutralization of acidic sediments.
3. Additions of base significantly reduced levels of Cu, Ni, Mn, Al and Zn in Middle, Lohi and Hannah Lakes. Metal concentrations in the lakes were controlled by pH-dependent solubility reactions, not by external input rates; hence, levels of Cu, Ni, Zn and Mn in Lohi Lake returned to pre-treatment levels after the lake re-acidified.
4. Additions of base produced no long-term changes in concentrations of TP or TN.

5. The addition of base was followed by an immediate and drastic reduction in phytoplankton standing stocks in Middle, Lohi and Hannah Lakes. Levels recovered to approach, but not exceed, pre-treatment levels within a few months. While taxa that are characteristically dominant in non-acidic lakes (chrysophytes) replaced acid-tolerant species (dinoflagellates) after community biomasses recovered, community diversities remained well below normal for the duration of the study. Dinoflagellates did not replace chrysophytes after the re-acidification of Lohi Lake, indicating that there is at least a 2-year lag before communities typical of acidic lakes are re-established.
6. Secchi transparency increased immediately after additions of base, accompanying the large decrease in phytoplankton standing stocks. In the long-term, however, Secchi transparency decreased by 2m in Lohi Lake after neutralization, then increased to pre-neutralization levels after the lake re-acidified. These longer term changes were not correlated with changes in phytoplankton standing stocks. The decrease in transparency after neutralization resulted in a shallower mixing zone and a cooler hypolimnion. It also reduced the depth of maximum photosynthetic activity.
7. Additions of base drastically reduced zooplankton standing stocks in Middle, Hannah and Lohi Lakes. Biomass did not recover for 2 years in Lohi Lake and communities typical of non-acidic lakes had not been re-established 4 years after the additions of base, when the lake re-acidified.
8. Rainbow trout were placed in submerged enclosures in Middle and Lohi Lakes after additions of base. They survived for less

than 4 days, on average. Despite the reduction in levels of trace metals that had occurred after additions of base, levels of metals, especially Cu, were too high to allow survival of the fish.

9. Additions of base raised the pH of Nelson Lake from 5.7 to 6.3. The addition significantly reduced levels of Cu, Ni, Mn, Al and Zn, but produced no short or long-term changes in nutrient chemistry or in assemblages of plankton.

Chapter 7: Experimental fertilizaton of lakes near Sudbury, Ontario

1. Phosphorus was added to Middle and Hannah Lakes from 1975 to 1978 and from 1976 to 1978, respectively. Phosphorus (at much higher rates of supply) and nitrogen were added to non-acidic (pH ≃6.0) Labelle Lake from 1977 to 1978 and to acidic (pH≃4.6) Mountaintop Lake from 1976 to 1978. Experimental additions provided >97% of the phosphorus supplied over the period of fertilization to Mountaintop and Labelle Lakes, 82-87% in Middle Lake and 79-82% in Hannah Lake.
2. Levels of TP increased in Middle and Hannah Lakes, but annual averages did not exceed 15 $\mu g\ L^{-1}$. Additions resulted in decreases of NO_3^- from 420 to 30 $\mu g\ L^{-1}$ in Middle Lake and from 520 to 90 $\mu g\ L^{-1}$ in Hannah Lake.
3. Phytoplankton biomass increased after additions of P. Chrysophytes were dominant in the spring in all years of fertilization, but dominant taxa in the summer were not predictable.
4. Zooplankton biomass was also increased by fertilization, but metal toxicity apparently limited the increase. Fertilization

did not encourage the re-establishment of communities typically observed in uncontaminated Precambrian Shield lakes.

5. Phosphorus budgets for Mountaintop and Labelle Lakes indicated that phosphorus was transported to the sediments as rapidly in acidic as in non-acidic lakes, even at very high rates of fertilization. Ratios of concentrations of N:P in Mountaintop and Labelle Lakes were 1.7-3.6 times higher than ratios of supply of N:P. This indicated that rates of loss of P from the water column were greater than rates of loss of N.
6. Differential uptake of NH_4^+ relative to NO_3^- was in part responsible for the decrease in epilimnetic pH that occurred over the summer in Mountaintop Lake. While pH normally increases in the euphotic zone of non-acidic lakes over the summer, in Mountaintop Lake it decreased, at one point to <4.0. In contrast, the pH of the hypolimnion increased to >6.0 at times of anoxia, most likely because of bacterial reduction of SO_4^{2-}, NO_3^- and ferric hydroxides. A portion of the generated alkalinity was re-entrained into the surficial waters at fall overturn.
7. Phytoplankton biomass increased substantially after fertilization in Mountaintop Lake, indicating that acidification of lakes will not prevent the development of the large phytoplankton standing stocks that characteristically accompany increased rates of nutrient supply. Temporal changes in species composition were much smaller in Mountaintop Lake than in Labelle Lake. A single species formed >90% of the community biomass for most of the ice-free season in each year.
8. Zooplankton densities increased in response to the increased phytoplankton food base in Labelle Lake. In the first year of

fertilization in Mountaintop Lake, zooplankton densities increased to levels much higher than ever observed in Labelle Lake. Levels of herbivorous zooplankton were, in fact, sufficiently high that their grazing activities reduced phytoplankton standing stocks to very low levels. Zooplankton densities decreased rapidly in the summer of the second year of fertilization in Mountaintop Lake and remained low (40 times lower than in the first year of fertilization) in the third fertilization season. Both the large increase in zooplankton biomass in the first year of fertilization and the crash in the second and third years in Mountaintop Lake were attributable to predator prey interactions. In 1976 densities of invertebrate predators were 40 times lower than in Labelle Lake, and zooplankton densities increased substantially in an environment virtually free of predation. Phytoplankton populations were decimated in consequence. In the second year of fertilization in Mountaintop Lake, increased prey availability in the absence of fish allowed the development of very substantial populations of *Chaoborus*. *Chaoborus* reduced zooplankton densities to very low levels. Acidification, therefore, indirectly reduced the resilience of the plankton communities of Mountaintop Lake to fertilization.

Chapter 8: Mass balance models - an explanation of the observed chemistry of lakes near Sudbury, Ontario

1. The concentrations of Mg^{2+}, K^+ and Na^+ in Clearwater and Lohi Lakes and Mg^{2+}, K^+, Na^+ and Cl^- in Nelson Lake were at steady state and were predictable using a simple mass

balance model. Mg^{2+} and K^+ concentrations appeared to be at steady state in Hannah and Middle Lakes, but predicted concentrations were much lower than measured concentrations, indicating that the inputs had been underestimated.

2. The Cl^- concentrations in Clearwater, Lohi, Middle and Hannah Lakes increased over the duration of the study as a result of treatment of roads in the lakes' watersheds with $CaCl_2$ and/or NaCl. Road applications were responsible for 95 to 98% of the total input of Cl^- to Middle and Hannah Lakes. The Ca^{2+} inputs associated with application of $CaCl_2$ were calculated from the Cl^- inputs not associated with Na^+.
3. Except for the third treatment in Lohi Lake, Ca^{2+} levels increased after neutralization by an amount expected on the basis of complete dissolution of added $CaCO_3$ and/or $Ca(OH)_2$. After corrections for extra inputs of Ca^{2+} associated with $CaCl_2$, levels in Clearwater and Lohi Lakes subsequently declined according to a simple washout model. The concentration of Ca^{2+} in Hannah and Middle Lakes was greater than predicted; hence, Ca^{2+} inputs used to make the prediction must have been underestimates.
4. The measured input of mineral acidity to Clearwater Lake in 1977-78 was sufficient to maintain the lake's alkalinity at ~-50 μeq L^{-1} (pH ~4.3), very near the measured concentration. The pH of the lake will not increase unless this input of acidity is reduced.
5. Predictions based on the mass balance model indicated that Lohi Lake would re-acidify (ie. have no remaining acid neutralizing capacity or ANC) in late 1976. Re-acidification occurred only 6-9 months later. The alkalinity of the lake stabilized at

~-15 μeq L^{-1}, 20-30 μeq L^{-1} greater than predicted, indicating that there was an unmeasured internal generation of ANC or that the inputs of mineral acidity were overestimated.

6. The measured ANC in Middle and Hannah Lakes were always much greater than ANC predicted by the mass balance model. Residual ANC would have been exhausted in mid to late 1978 in Hannah Lake and in mid 1975 in Middle Lake according to the model. In Hannah Lake, measured ANC was, in fact, higher in late 1978 than immediately after neutralization. ANC supplied by NO_3^- uptake by the biota following fertilization could account for only 4-12% and 11-46% of the extra ANC generated in Hannah and Middle Lakes, respectively. It was hypothesized that the remainder of the ANC was released from the sediments which had been previously neutralized by the additions of $CaCO_3/Ca(OH)_2$.
7. The measured inputs of SO_4^{2-} to Clearwater and Lohi Lakes could not account for the observed concentrations in the lakes. An additional input of SO_2 to the lakes' surfaces that was not measured in the bulk deposition collectors was the source of the extra SO_4^{2-}. The bulk deposition measurements accounted for only 33% of the total input of SO_4^{2-} and SO_4^{2-}-producing substances to the whole watersheds (40% to the terrestrial portion and 24% to the lake surfaces). Similarly, unmeasured SO_2 inputs to Middle and Hannah Lakes accounted for 66 to 80% of the total.
8. The concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) in Hannah and Middle Lakes were much greater than predicted using the measured or estimated mass balances and steady-state model. Calculation of the inputs from the

watersheds required to achieve the observed lakes concentrations allowed estimation of the input of strong acids to the watersheds. This calculated input was much greater than the measured bulk deposition of strong acids by an amount almost identical to the "additional" SO_4^{2-} predicted by the SO_4^{2-} mass balances.

9. Comparison of 4 different methods of calculating the excess acid deposition demonstrated that;
   a) all results were in good agreement
   b) the unmeasured acid input was H_2SO_4 derived from oxidation of dry deposited SO_2, and
   c) this component of the acid input was larger than all other measured components, being ~70 , ~85 and ~67% of the total input for the Middle, Hannah and Clearwater Lake watersheds, respectively. It was demonstrated in Chapter 5 that ~50% of the total input of strong acid to the Nelson Lake watershed was unmeasured.
10. In the acidic lakes (Clearwater and Lohi), Cu, Ni and Al behaved as conservative substances. There concentrations were accurately predicted by the same mass balance model that was used for major ions. Reductions in inputs required to meet accepted standard concentrations are 95% for Cu, 90% for Ni, 55% for Zn, 65% for Fe and ~ 70% for Al. These proposed reductions do not take into account the beneficial effects on metal concentrations that would result if the lake pH was concurrently increased. On the other hand, the acceptable concentrations may be too great because they were proposed for hard-water lakes. In the non-acidic lakes (Hannah, Middle and Nelson), much of the input of Cu, Ni, Zn, Al and Fe was

retained in the lakes' sediments. Estimated reductions in input needed to meet accepted criteria are as high as 99% for Cu, 97% for Ni, 61% for Zn, 48% for Fe and 69% for Al.

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INTRODUCTION

Over the past century, mining, smelting and ancillary lumbering activities in and around Sudbury, Ontario, have resulted in devastation of a large area of forest (Linzon 1978, Hutchinson 1979). Gorham and Gordon (1960) were the first to observe that lakes and ponds were also affected. Many lakes within 24 km of Sudbury had elevated sulphate levels and reduced pH. Subsequently, Beamish and Harvey (1972) noted that 70 of 150 lakes in the La Cloche Mountains, 50-100 km southwest of Sudbury, had pH less than 5.5, with 33 of these having pH less than 4.5. Conroy _et_ _al_. (1974) observed that many lakes equally distant from Sudbury in a northeasterly direction were also acidic. Because one of the world's largest point sources of emissions of SO_2 is located in Copper Cliff, west of Sudbury, and because prevailing ground level winds in Sudbury are from the northeast and southwest acidification of these lakes was attributed to local industrial activities.

Johnson and Owen (1966) noted that many lakes in the Sudbury area were also contaminated with toxic trace metals, especially copper and nickel. Large quantities of copper, nickel, and other trace metals are discharged into the atmosphere by local industries (Conroy _et_ _al_. 1974).

The Ontario Ministry of the Environment (in cooperation with the Ontario Ministry of Natural Resources) initiated a research program in 1973 called the Sudbury Environmental Study (SES). The overall objective of the program was to develop criteria for the management of atmospheric emissions from the mining/smelting industries located in metropolitan Sudbury. The specific objectives of the Limnology Unit of the Water Resources Branch of the Ministry of the

Environment were as follows:

1. to determine the causes for the observed chemistry and biology of Sudbury-area lakes,
2. to conduct experiments to define rate processes associated with the acidification of Sudbury-area lakes and thereby contribute to the development of empirical models that could be used to predict consequences of changes in locally-based emissions,
3. to develop reclamation techniques which could be applied to economically important lakes to bring about improvements in water quality and subsequently in the fisheries, regardless of changes in rates of inputs of acids.

The structure of this report reflects three major approaches that were adopted to address these general objectives. These approaches were:

1. measurement of current atmospheric deposition of pollutant substances and examination of historical loadings of substances recorded in the sediments of lakes,
2. quantitative manipulation of the chemistry of whole lakes,
3. construction of mass balances or material budgets for the lakes and their watersheds.

Processes that have occurred in a lake, its watershed and airshed over the lifespan of the lake may be recorded in the lake's sediments. By determining the age of different sediment layers, the corresponding sediment chemistry can be used to accurately date events that may have affected the lake. A chronology of past events determined from analyses of the sediments of the study lakes is discussed in Chapter 3. The purposes for examining the sediments were:

1. to determine current and past accumulation rates of materials in

lake sediments in the Sudbury area and determine if elevation of copper, nickel or other trace metal concentrations coincided in time with the initiation of smelter operations in the area,

2. to determine if the sediments recorded any other important changes in lake chemistry or biology and to determine if these changes were consistent with the timing of the input of strong acids,
3. to determine if whole-lake manipulation experiments affected the lake sediments.

Whole-lake manipulation experiments have been extremely important in elucidating the central importance of phosphorus loading in the eutropication of lakes (Schindler and Fee 1974). Schindler *et al*. (1980) recently demonstrated that such experiments might be equally important in documenting changes accompanying the acidification of lakes. Whole-lake experiments involving additions of nutrients and/or base are discussed in Chapters 6 and 7 of this report. They were designed with the following specific purposes:

4. to quantify processes consuming acid neutralizing capacity in acidified, metal-contaminated lakes,
5. to determine effects of base additions on transparency and on nutrient, major ion and trace metal chemistry in Sudbury-area lakes, and to determine rates and extent of "recovery" of plankton that could accompany an increase in lake pH,
6. to determine if water quality would be suitable for survival of fish following additions of base,
7. to determine the extent to which biological processes could influence lake pH or acid neutralizing capacity,
8. to determine if acidification would alter the response of phytoplankton to increased rates of nutrient supply,

9. to determine if fertilization would increase rates of recovery of biota after additions of base.

A mass balance for a substance is an accounting of the magnitude of the fluxes of the substance into and out of a lake or watershed. Mass balances were measured for the study lakes to allow quantification of rate processes associated with acidification. Recent (Chapter 2) input rates of materials were calculated. Combined with measured hydrological regimes of the lakes (Chapter 4), input rates from watersheds to the lakes were calculated (Chapter 5) and used as inputs to mass balance calculations for the lakes (Chapter 8). These chapters, therefore, describe studies with the following specific objectives:

10. to determine deposition rates, from the atmosphere to the drainage basins of the study lakes, of major ions, including H^+, nutrients and trace metals,
11. to determine the influence of local industrial operations on these deposition rates,
12. to provide hydrological data needed for the construction of mass balances for the study lakes and their watersheds,
13. to determine the factors controlling the chemistry of tributaries to the lakes,
14. to determine the gross export of materials from the watersheds, the quantities of and factors controlling the retention of materials within watersheds and; hence, estimate the net rate of export of materials from the watersheds,
15. to determine if major ion chemistry of the lakes could be explained by measured mass balances,
16. to determine if chemical consequences of additions of base were predictable,

17. to determine rates of re-acidification of neutralized lakes,
18. to determine if additions of nutrients affect rates of re-acidification,
19. to determine reductions of inputs of acid and trace metals required to provide acceptable water quality.

Large amounts of physical, chemical and biological data were collected from a small number of lakes in the Sudbury area to satisfy these objectives. Such long-term data collections are rare for Precambrian Shield lakes and in the limnological literature in general. These data, together with a geochemical description of the watersheds, morphometric data for the lakes and sampling methodologies employed in the study are summarized in Volume II of this report.

CHAPTER 1

CHARACTERIZATION OF LAKES NEAR SUDBURY, ONTARIO

N.D. Yan and G.E. Miller

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A. Introduction

In the summer of 1973, intensive monitoring was initiated on Middle, Hannah, Lohi and Clearwater Lakes, four acidic lakes in the Sudbury area. Two of the lakes were neutralized in the fall of 1973, and these neutralization experiments were the first experiments performed under the auspices of the Sudbury Environmental Study (SES). Between 1975 and 1977 the objectives of the study were expanded and studies on three more lakes (Nelson, Mountaintop and Labelle) were initiated in consequence. Various studies on these seven lakes, the results of which are described in the remaining chapters of this report, were continued until 1979. In this chapter the initial physical, chemical and biological character of the lakes is described.

From 1973 to 1979 Clearwater Lake was monitored as a reference for manipulation experiments performed in other lakes, and to provide information on seasonal and longer term variability in the chemistry and biota of an acidic lake. In this chapter, limnological conditions in Clearwater Lake are compared with the other intensively studied Sudbury-area lakes, with 2 less intensively studied SES lakes, Swan and Joe Lakes, and with six lakes in the Haliburton and Muskoka areas of central Ontario, with pH 5.7-6.6, namely, Blue Chalk, Red Chalk, Chub, Dickie, Harp and Jerry Lakes (Dillon _et_ _al_. unpub data). This chapter will serve mainly as a summary of previous descriptions of the character of the SES Lakes (see especially Scheider _et_ _al_. 1975, Scheider and Dillon 1976, Yan _et_ _al_. 1977, Yan 1979, Dillon _et_ _al_. 1979, Yan and Strus 1980, Harvey _et_ _al_. 1981).

The location of the study lakes is indicated in Fig. 1-1. Their morphometry and distance from Copper Cliff are summarized in

Table 1-1. The lakes vary in surface area (5 to 309 ha) and maximum depth (9-51 m) by amounts that are typical of Precambrian Shield lakes (Brunskill and Schindler 1971). Joe and Nelson Lakes are multiple basin lakes while the remaining lakes have a single basin. Hydrological regimes of the lakes are discussed in **Chapter 4.** Surficial and bedrock geology and other watershed characteristics of the lakes are described in Appendix 2.

Human usage of the lakes is primarily recreational. Several cottages and permanent dwellings are located in the watersheds of Middle, Hannah, Lohi, Clearwater and Nelson Lakes. One summer camp is located at each of Nelson and Hannah Lakes. There is no development in the Mountaintop or Labelle Lake watersheds.

B. Temperature Clarity and Oxygen

The thermal regimes of lakes are determined by a complex interaction of factors including insolation, wind, morphometry, watershed topography, fetch, etc. (Ragotzkie 1978). North temperate lakes are usually dimictic or, if shallow (<8m), holomictic. Isotherm diagrams for all study lakes excluding Joe and Swan Lakes, are included in Appendix 5. Hannah Lake, the shallowest lake, was holomictic in all years as was Middle Lake in 1973. Middle Lake in other years (1974-1979) and all other lakes in all years (1973-1979) were dimictic. Early spring oxygen profiles (Appendix 5) indicated that spring overturn was incomplete in Mountaintop and Labelle Lakes and in the northwest basin of Nelson Lake (Station 4). These lake basins are all small and well-protected and spring overturn is frequently incomplete in such water bodies. All other lakes mixed completely in the spring.

The waters of Clearwater Lake are very clear (extinction coefficient $\eta = 0.13 m^{-1}$) in comparison with the six non-acidic

Table 1-1: Summary of morphometric data for SES study lakes. Notations after Hutchinson (1957). Distances from Copper Cliff are indicated. Certain parameters were not determined (ND).

	Distance from Copper Cliff (km)	Lake Drainage Area A_d (ha)	Lake Area A_o (ha)	Lake Volume V ($10^5 m^3$)	Mean Depth $\bar{z}$ (m)	Maximum Depth z_{max} (m)	Shoreline Length L (km)	Development of Shoreline D_L	Development of Volume D_V
Hannah	4.3	76	27.3	10.8	4.0	8.5	2.70	1.46	1.40
Middle	5.0	250	28.2	17.5	6.2	15.0	3.20	1.70	1.24
Loni	11	460	40.5	25.0	6.2	19.5	4.47	1.98	0.95
Swan	13	ND	5.78	1.62	2.8	8.8	1.59	1.87	0.96
Clearwater	13	340	76.5	64.2	8.3	21.5	4.97	1.60	1.20
Labelle	27	173	6.16	2.36	3.8	10.2	1.32	1.50	1.18
Nelson	28	798	309	359	11.6	51.0	33.3	5.35	0.68
Joe	29	ND	180	201	11.2	34.0	14.2	2.99	0.99
Mountaintop	52	86	4.9	2.07	4.3	9.5	1.03	1.31	1.36

Muskoka-Haliburton lakes (η is 0.33 - 0.99m^{-1}, Harvey et al. 1981). Harvey and coworkers attributed the increased clarity to precipitation of organic matter by aluminum.

In Clearwater Lake increased light penetration has resulted in changes in the lake's thermal regime. The epilimnion of the lake (pH ~4.3) was usually 10-12 m thick (Fig. 1-2), much thicker than the epilimnia of non-acidic Precambrian lakes of similar size. The epilimnion of Blue Chalk Lake, a non-acidic lake (pH ≈6.5) in south-central Ontario was only 5-7 m thick, for example (Harvey et al. 1981). The area (A_0), length (L) and mean breadth ($\bar{b}$) of Blue Chalk Lake are 49.4 ha, 1600 m and 310 m, respectively. These are quite similar to Clearwater Lake, for which A_0 is 76.5 ha, L is 2000 m and $\bar{b}$ is 380 m.

A second consequence of increased clarity is a warmer hypolimnion. The average temperature of the hypolimnion of Clearwater Lake was 14.5°C (Fig. 1-2). The hypolimnetic temperature of relatively deep, non-acidic north temperate lakes is more commonly 4-6°C (Schindler 1971). Because of the deeper epilimnion and warmer hypolimnion, more heat is stored in Clearwater Lake than in morphometrically similar non-acidic lakes. Harvey et al. (1981) noted that the average maximum amount of heat stored in Clearwater Lake in the summer was 16.1 kcal cm^{-2} (±0.3, 95% confidence limits). This was significantly higher than the maximum amount of heat stored in Blue Chalk Lake (14.5 ± 0.25 kcal cm^{-2}).

Because of the warmer hypolimnion and thicker epilimnion, fall overturn occurred in Clearwater Lake in mid-September in all years (Fig. 1-2), 4-8 weeks earlier than fall overturn in non-acidic Blue Chalk Lake (Dillon et al., unpub. data). An earlier fall overturn may prevent hypolimnetic anoxia in acidic lakes that have small ratios of hypolimnia to epilimnia or experience incomplete spring overturn.

Oxygen regimes in lakes are influenced by the productivity of the biota and by temperature, morphometry and water clarity. Schindler (1971) observed that deep, clear Shield lakes have positive heterograde oxygen profiles. Vertical oxygen profiles were also positive heterograde in all SES lakes with the exception of Hannah Lake which was holomictic (Appendix 5). The great clarity of Clearwater Lake facilitated production of oxygen by the phytoplankton at depths greater than normally possible in Precambrian Shield lakes. Vertical chlorophyll profiles indicated that phytoplankton did accumulate in the profundal waters of the lake (Fig. 1-3). Oxygen maxima were observed at depths of approximately 14m (Fig. 1-4), indicating that the phytoplankton were within the euphotic zone and were productive. Levels of photosynthetically active irradiance were remarkably high at that depth, i.e. 16% of surface levels ($\eta = 0.13m^{-1}$).

C. Chemistry

i. Average Concentrations of Major Ions, Nutrients and Trace Metals

Harvey *et al*. (1981) presented a review of the changes in major ion chemistry of Canadian Precambrian Shield lakes accompanying their acidification. Data from non-acidic lakes in northwestern and southcentral Ontario have been taken from this review and are compared with the major ion content of Clearwater Lake in Table 1-2. On an equivalent basis the concentration of major cations decreased in the order $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ in the non-acidic lakes. This is a reflection of the fact that Ca- and Mg-rich minerals are more abundant and more easily weathered than Na-

Table 1-2: Conductivity and major ion content (μeq L^{-1}) in Clearwater Lake (1973 to 1979) compared to 40 lakes in the Experimental Lakes Area (Armstrong and Schindler 1971) and 14 lakes in the Muskoka-Haliburton region of Ontario (Harvey *et al*. 1981). Data are whole lake composites. (Standard error in parenthesis).

	Clearwater Lake								
	1973	1974[1]	1975	1976	1977	1978	1979	ELA	Muskoka Haliburton
Conductivity (μmhos cm^{-1})	89	86	85	87	89	83	85	19	33
H^+	51 (3.2)	58 (2.4)	47 (1.6)	59 (2.5)	79 (5.2)	40 (1.8)	39 (4.5)	<1	<1
Ca^{2+}	315 (8.0)	275 (3.0)	275 (5.5)	305 (13)	285 (4.5)	285 (3.0)	315 (7.0)	80	150
Mg^{2+}	156 (25)	107 (4.9)	90 (4.1)	139 (9.8)	115 (8.2)	123 (4.1)	115 (2.5)	74	72
Na^+	61 (7.8)	65 (2.6)	70 (3.9)	65 (1.3)	70 (1.3)	70 (0.9)	74 (2.6)	39	36
K^+	33 (4.6)	26 (0.8)	22 (2.3)	18 (0.3)	18 (0.3)	17 (0.8)	18 (0.3)	10	13
Σcations	616	531	504	586	567	535	561	203	271
SO_4^{2-}	579 (6.5)	533 (8.5)	519 (14)	542 (6.7)	550 (6.5)	498 (4.0)	458 (3.8)	63	170
CL^-	not sampled	31 (1.1)	42 (1.1)	51 (0.8)	62 (1.4)	87 (1.7)	102 (1.4)	39	18
NO_3^--N	8 (0.3)	5 (0.4)	5 (0.3)	4 (0.6)	4 (0.3)	6 (0.2)	5 (0.3)	-	-
HCO_3^-	0	0	0	0	0	0	0	62	110
Σanions		569	566	597	616	591	565	164	298

[1] 1 m below surface sample

or K-rich minerals in the Precambrian Shield. In these non-acidic lakes H^+ is quantitatively unimportant. Excluding H^+, the order of importance of major cations was similar in Clearwater Lake; however, levels of all cations were much higher than in the non-acidic ELA or Muskoka-Haliburton lakes (Table 1-2). Reasons for the increased levels of cations, including human activities within the lake's watershed (deicing, road construction, dust control) and accelerated weathering of watershed materials attributable to the deposition of strong acids, are described in detail in later chapters of this report.

Major ion contents of all of the SES study lakes are given in Table 1-3. As in Clearwater Lake, the equivalent concentration of major cations, excluding H^+, decreased in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ in the acidic and non-acidic lakes. Levels decreased with distance from Sudbury, mainly because of increased rates of weathering in watersheds of lakes close to Sudbury (see Chapter 5). Levels of cations in Mountaintop Lake, the most distant of the study lakes from Sudbury, were as low as those in non-acidic lakes in Muskoka and Haliburton, but they were higher than in lakes in northwestern Ontario (Table 1-2). Harvey _et_ _al_. (1981) suggested that deposition of strong acid has increased concentrations of Ca^{2+} in Muskoka-Haliburton lakes.

Clearwater Lake was acidic during all years of study. The concentration of H^+, averaged over the ice-free season, varied from a low of 39 $\mu eq\ L^{-1}$ in 1979 corresponding to a pH 4.41, to a high of 79 $\mu eq\ L^{-1}$ in 1977, corresponding to a pH of 4.1 (Table 1-2). Hannah, Middle, Lohi and Mountaintop Lakes were also very acidic with average H^+ concentrations of 51, 40, 41 and 24 $\mu eq\ L^{-1}$, respectively (Table 1-3). Nelson Lake (pH 5.7) and Labelle

Table 1-3: Conductivity and major ion content (μeq L^{-1}) of SES lakes (mean with standard error in parentheses). Distances from Sudbury are indicated.

	Hannah[1] 1974	Middle[2] 1973	Lohi[2] 1973	Clearwater[1] 1977	Labelle[3] 1977	Nelson-1[1] 1975	Mountaintop[3] 1976
Distance from Sudbury (km)	4.3	5.0	11	13	27	28	52
Conductivity (μmhos cm^{-1} 25°C)	166	131	88	89	51	46	45
Ca^{2+}	570 (5.0)	490 (7.5)	310 (5.0)	285 (4.5)	255 (6.5)	205 (3.0)	150 (16)
Mg^{2+}	295 (3.3)	410 (24)	205 (22)	115 (8.2)	91 (1.6)	82 (0)	82 (0)
Na^{+}	152 (7.8)	104 (7.8)	83 (6.5)	70 (1.3)	48 (1.3)	42 (1.7)	43 (0)
K^{+}	54 (2.0)	49 (4.3)	33 (2.3)	18 (0.3)	16 (0.5)	12 (0.3)	11 (0)
H^{+}	51 (3.0)	40 (2.9)	41 (1.9)	79 (5.2)	1 (0.2)	2 (0.2)	24 (2.7)
Σ^{+}	1120	1090	672	567	411	343	310
SO_4^{2-}	1200 (42)	927 (14)	556 (7.1)	550 (6.5)	325 (5.4)	329 (5.8)	292 (7.1)
CL^{-}	76 (3.4)	-	-	62 (1.4)	14 (0.6)	12 (0.6)	11 (0)
NO_3^{-}-N	41 (1.0)	32 (1.8)	6 (0.6)	4 (0.3)	2 (0.7)	2 (0.4)	3 (0.3)
HCO_3^{-}	0.2 (0.2)	0	0	0	76 (2.2)	40 (3.0)	11 (5.0)
Σ^{-}	1320	-	-	616	417	383	317

[1] in this and subsequent tables data from 1974, not 1973 in Hannah Lake, are employed as this was the last year before manipulations. Data from 1977 in Clearwater Lake are used as after this year the chemistry may have changed in response to a shutdown of operations of smelters in the Sudbury area

[2] pre-addition of base

[3] pre-addition of N and P

Lake (pH 5.95) were much less acidic than the other lakes, although they are at the lower end of the range of pH levels typically observed in clear Precambrian Shield lakes (Armstrong and Schindler 1971).

Bicarbonate is the dominant anion in Precambrian Shield lakes that have not been influenced by the atmospheric deposition of strong acid. When the depositon of acid sulphates increases the relative importance of SO_4^{2-} in lakes also increases. In ELA lakes SO_4^{2-} and HCO_3^- levels are approximately equal on an equivalent basis, while in non-acidic lakes in Muskoka-Haliburton SO_4^{2-} concentrations are almost twice as high as HCO_3^- concentrations (Table 1-2). SO_4^{2-} exceeded HCO_3^- by even greater amounts in Labelle Lake (4-fold) and in Nelson Lake (8-fold), and it replaced HCO_3^- in Clearwater, Middle, Lohi, Hannah and Mountaintop Lakes, the acidic SES lakes (Table 1-3).

Levels of total Cu, Ni, Zn, Al and Mn were exceptionally high in Clearwater Lake (Table 1-4). At the low pH, much of the Al would be present as Al^{3+}, perhaps accounting for the missing cations especially in 1975, 1977 and 1978 (Table 1-2). Levels of metals were lowest in 1978 and 1979, most likely because of decreased rates of input to the lake during the shutdown of INCO operations between September 1978 and June 1979 (see Chapter 2). Levels of Al and Mn are elevated in acidic lakes in Ontario that are not close to centres of industrial activity (Beamish and Van Loon 1977, Scheider _et_ _al_. 1979a). Levels of Zn, Cu and Ni are elevated only in acidified lakes near Sudbury, and are attributable to industrial operations in the area (see chapter 3).

In waters with low levels of organic matter, the speciation of copper is mainly determined by the concentration of carbonate and

Table 1-4: Concentrations of metals ($mg\ m^{-3}$) in Clearwater Lake, 1973-79 (mean with standard error in parenthesis). All values are whole lake composites unless otherwise indicated.

	1973[1]	1974[2]	1975	1976	1977	1978	1979
Cu	98.3 (2.6)	101 (4.0)	100 (3.6)	91.4 (3.1)	81.3 (4.4)	74.4 (1.2)	59.8 (3.8)
Ni	283 (6.3)	289 (5.9)	272 (4.3)	271 (5.9)	278 (7.0)	257 (4.0)	220 (7.8)
Zn	47.9 (4.6)	46.7 (1.7)	49.0 (3.7)	54.9 (4.7)	39.2 (2.5)	37.3 (0.66)	31.4 (1.7)
Fe	114 (16.1)	93.9 (13.6)	132 (11.1)	94.1 (11.8)	88.2 (7.5)	57.1 (3.5)	55.0 (4.3)
Al	420 –	516 (43.0)	447 (10.6)	397 (21.6)	381 (9.5)	324 (8.5)	272 (19.3)
Mn	328 (5.3)	310 (10.7)	289 (2.9)	301 (6.9)	290 (6.0)	297 (2.5)	282 (3.1)
labile Cu	–	–	63.4 (4.8)	64.7 (5.0)	63.0 (9.9)	43.8 (5.9)	–
labile Zn	–	–	39.5 (3.4)	38.8 (11.2)	29.4 (6.9)	21.0 (3.4)	–

---

1 m above bottom

[2] 1 m below surface

[3] determined by anodic stripping voltometry

hydroxide ions (Pagenkopf et al. 1974). Because of low pH (and hence of low concentrations of inorganic carbon, hydroxide and dissolved organic matter) between 50 and 80% of the total Cu (t-Cu) and t-Zn in Clearwater Lake was labile, as determined by anodic stripping voltometry (Table 1-4). In Clearwater Lake, approximately equal fractions of the Zn and Cu were labile. In contrast, Chau and Lum-Shue-Chan (1974) determined that larger fractions of Zn than Cu were labile in 15 lakes near Sudbury. Labile Zn was observed in all lakes. Labile Cu was observed in only 3 of the lakes, in the lake with the highest concentration of t-Cu (46 $\mu g\ L^{-1}$) and in the only 2 lakes with pH <5.0. In all other lakes, the pH was >6.0 (Chau and Lum-Shue-Chan 1974).

With the exception of Fe which is a major lithological element, levels of metals in the study lakes decreased with increasing distance from Sudbury (Table 1-5). This phenomenon has been previously demonstrated (Anon. 1978). However, even at Mountaintop Lake, 50 km from Sudbury, levels of Zn, Cu and Ni were much higher than observed in Muskoka-Haliburton lakes (<2 $\mu g\ L^{-1}$ of Cu and Ni and 5 $\mu g\ L^{-1}$ of Zn). Levels of Fe, Al and Mn in Labelle and Nelson Lakes, the 2 non-acidified lakes, were within the range typically observed for Muskoka-Haliburton lakes receiving precipitation with an average pH of ≃4.0 (Table 1-5).

Ice-free period average levels of total phosphorus (TP) varied from 2.4 to 5.9 $\mu g\ L^{-1}$ from 1973 to 1979 in Clearwater Lake (Table 1-6). These levels are typical of soft-water Precambrian Shield lakes (Armstrong and Schindler 1971, Anon. 1978). Ratios of total nitrogen (TN) to TP ranged from 25:1 to 80:1 in Clearwater Lake, indicating that P was the element present in shortest supply (Schindler 1977). Levels of TP (4.6 to 10.7 $\mu g\ L^{-1}$) and TN/TP

Table 1-5: Metal concentrations (mg m^{-3} mean with standard error in parentheses) in SES lakes. 1976-1978 averages (range in brackets) from 15 lakes in Muskoka-Haliburton from Dillon (unpub. data) are presented for comparison. Distances of lakes from Sudbury are indicated. Data for 1973 are 1 m above bottom, 1m below surface for 1974, and are whole lake estimates for other years.

	Hannah 1974	Middle[1] 1973	Lohi[1] 1973	Clearwater 1977	Labelle[2] 1977	Nelson-1[1] 1975	Mountaintop[2] 1976	Muskoka-Haliburton 1976-1978
Distance from Sudbury (km)	4.3	5.0	11	13	27	28	52	214
Cu	1108 (17.8)	496 (6.9)	83.6 (5.6)	81.3 (4.4)	4.8 (1.7)	22.0 (3.0)	24.0 (2.0)	<2
Ni	1865 (76.1)	1068 (17.6)	254 (10.3)	278 (7.0)	12.7 (1.6)	17.1 (0.9)	12.2 (1.6)	<2
Zn	120 (4.3)	91.3 (10.3)	41.6 (5.7)	39.2 (2.5)	10.6 (1.3)	18.3 (1.2)	28.0 (3.1)	5 (3-8)
Fe	47.0 (7.6)	143 (14.9)	320(90[3]) (85.6)	88.2 (7.5)	73.0 (8.5)	60.8 (12.9)	215 (33.8)	98 (20-230)
Al	1097 (61.4)	-	-	381 (9.5)	73.3 (13.2)	86.6 (5.7)	440 -	42 (8-91)
Mn	340 (12.3)	354 (10.3)	284 (10.4)	290 (6.0)	74.8 (10.3)	63.1 (1.8)	120 -	33 (15-71)

---

[1] prior to additions of base

[2] prior to additions of N and P

[3] 1m above bottom levels of Fe were possibly affected by anoxic sediment surface. This value is the single whole lake composite value before additions of base

Table 1-6: Concentrations of nutrients (mg m^{-3}) and nutrient ratios in Clearwater Lake, 1973-79 (mean with standard error in parenthesis). All values are whole lake composites unless otherwise indicated.

	1973	1974[1]	1975	1976	1977	1978	1979
TP	5.9	5.5	4.1	5.2	6.5	4.6	2.4
	(0.57)	(0.83)	(0.89)	(0.74)	(0.74)	(0.52)	(0.08)
TKN	131	84.4	144	132	102	128	116
	(8.3)	(1.2)	(3.4)	(2.0)	(5.3)	(5.4)	(4.1)
NO_3^--N[2]	108	65.4	64.0	53.3	61.6	86.0	75.8
	(4.6)	(5.1)	(4.5)	(8.0)	(3.8)	(2.5)	(3.5)
NH_4^+-N	35.0	14.8	22.0	25.7	36.2	33.5	32.2
	(8.3)	(1.2)	(3.4)	(2.0)	(5.3)	(5.4)	(4.1)
TIN[3]/TN	0.60	0.54	0.41	0.43	0.60	0.56	0.56
TN/TP	40.5	27.3	50.7	35.6	25.2	46.5	79.6

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[1] 1 m below surface

[2] includes NO_2^- in this and all subsequent tables

[3] total inorganic nitrogen (TIN) = $NH_4^+ + NO_2^- + NO_3^-$

ratios (25:1 to 127:1) in the other study lakes were similar to those of Clearwater Lake (Table 1-6 and 1-7).

Concentrations of NO_3^- are generally very low in Precambrian Shield lakes. Nitrate is efficiently retained within watersheds and assimilated rapidly in lakes by plankton during the growing season. Nitrate levels varied from 53 to 108 μgL^{-1} in Clearwater Lake, much higher than in Nelson and Labelle Lakes, the non-acidic study lakes (Table 1-7). The lakes closest to Sudbury (Middle and Hannah) had remarkably high average NO_3^--N levels of 442 and 576 μgL^{-1}. The watersheds of Middle and Hannah Lakes are comprised mainly of exposed bedrock. Both soil and vegetation are scanty (Appendix 2C). High levels of NO_3^- in these lakes are perhaps a reflection of the reduced capability of the watersheds to retain NO_3^-.

ii. Changes in Chemistry with Depth

Concentrations of major ions did not change significantly with depth in Clearwater Lake (Appendix 6). Concentrations of NO_3^--N in six non-acidic, oligotrophic lakes in south-central Ontario increased with depth because of algal uptake of NO_3^- in the surficial waters. Levels in the epilimnion of Clearwater Lake were higher than those of all of the non-acidic lakes, and they decreased with depth, a clear inversion of the pattern in the non-acidic lake. (Table 1-8). Levels of NO_3^--N were equivalent in the epi-, meta- and hypolimnion after spring overturn in Clearwater Lake, but NO_3^- was depleted over the growing season in the hypolimnion (Fig. 1-5). The concentration of phytoplankton biomass in these deep strata (Fig. 1-4) and their activity, as indicated by deep oxygen maxima (Fig. 1-3), suggest that the seasonal decline in NO_3^- levels in the profundal waters is

Table 1-7: Concentrations of nutrients (mg m^{-3}) and nutrient ratios in SES lakes (mean with standard error in parenthesis). All values are whole lake composites unless otherwise indicated.

	Hannah[3] 1974	Middle[1] 1973	Lohi[1] 1973	Clearwater 1977	Labelle[2] 1977	Nelson-1[1] 1975	Mountaintop[2] 1976
Distance from Sudbury (km)	4.3	5.0	11	13	27	28	52
TP	5.7 (0.79)	7.3 (1.4)	6.1 (1.0)	6.5 (0.74)	10.7 (1.1)	4.6 (0.78)	6.4 (0.84)
TKN	150 (15.2)	180 (17.0)	193 (18.3)	102 (5.3)	256 (22.6)	178 (8.5)	191 (16.3)
NO_3^--N	576 (23.1)	442 (24.8)	76.9 (8.7)	61.6 (3.8)	20.3 (10.2)	21.3 (5.1)	36.5 (3.5)
NH_4^+-N	17.3 (3.6)	38.0 (6.6)	68.6 (8.8)	36.2 (5.3)	24.6 (5.6)	18.9 (2.0)	24.1 (3.1)
TIN/TN	0.82	0.77	0.54	0.60	0.16	0.20	0.27
TN/TP	127.	85.2	44.2	25.2	25.8	43.3	35.5

[1] prior to additions of base
[2] prior to additions of N and P
[3] values are 1 m below surface

Table 1-8: Average concentrations of NO_3^--N ($\mu g L^{-1}$) in epi-, meta- and hypolimnion of Clearwater Lake (1979) and of 6 lakes in Muskoka-Haliburton (1976-1979, Dillon *et al.* unpub. data). Extinction coefficients (η in ln units m^{-1}) measured in 1976 are presented.

	Clearwater	Blue Chalk	Red Chalk	Jerry	Dickie	Chub	Harp
epilimnion	54	8	31	37	22	19	10
metalimnion	31	10	60	129	36	60	34
hypolimnion	19	37	129	202	70	83	120
η	0.13	0.33	0.41	0.62	0.99	0.81	0.56

attributable to uptake of NO_3^- by the phytoplankton. Losses through denitrification were unlikely as the hypolimnion was well oxygenated. The increased clarity indirectly resulting from acidification of Clearwater Lake (Table 1-8) has a profound effect on vertical distribution of phytoplankton and, therefore, influences vertical profiles of nutrients.

An accumulation of phytoplankton at the lower limit of the euphotic zone is characteristic of stratified Precambrian Shield lakes. In experimentally fertilized lakes in northwestern Ontario, Fee (1976) observed massive accumulations of large colonial chrysophytes at depths representing 0.3 - 3.5% of surface photosynthetically active radiation (PhAR). While chlorophyll concentrations within these bands were often 2 orders of magnitude higher than epilimnetic concentrations, Fee (1978) concluded that these populations made only a small contribution to whole lake productivity. This conclusion was probably also applicable to Clearwater Lake as chlorophyll concentrations in the hypolimnion were only a few times greater than epilimnetic concentrations (Fig. 1-4).

Dinoflagellates are the most important phytoplankters in Clearwater Lake (to be discussed). These organisms are known to accumulate in or migrate to the deeper waters of clear non-acidic lakes at mid-day, for example, _Glenodinium neglectum_ in Waldo Lake in Oregon (Larson 1978) and _Gymnodinium uberrimum_ in Vorderer Finstertaler See (Tilzer 1973). Dinoflagellates are generally considered to be negatively phototaxic, moving with rates often in excess of 1 m hr^{-1}. No studies have been performed on vertical migration rates of dinoflagellates in highly acidic lakes, although Waldo Lake is at equilibrium with atmospheric CO_2 and has a pH of ~5.6 (Malueg _et al_. 1972). The frequent observations of accumulations of dinoflagellates at great depths in non-acidic lakes, however, suggest that dinoflagellates formed the deep chlorophyll maxima in Clearwater Lake.

Vertical variations in concentrations of some metals were also evident in Clearwater Lake. Levels of all metals were more or less constant over the ice-free season in the epi- and metalimnion, but levels of Ni and Zn (Appendix 6) and especially Cu decreased over the ice-free season in the hypolimnion while concentrations of Fe increased (Fig. 1-6). Decreases in Cu were most likely attributable to uptake by the biota followed by sedimentation of the algae (Mierle pers. comm.). Greatest increases in hypolimnetic concentrations of Fe (Fig. 1-6) and NH_4^+ (Fig. 1-5) occurred in early September, 1979, just before autumnal overturn. Levels of oxygen were 3.3 mg L^{-1} at a depth of 19 m at this time, the lowest levels ever observed (Fig. 1-3). The increases in Fe and NH_4^+ concentrations suggest that at that time the sediment surface may have been anoxic.

D. Primary Producers

i. Phytoplankton

Phytoplankton communities of Lohi, Middle, Hannah, Nelson and Clearwater Lakes have been discussed in detail in previous publications (Scheider _et_ _al_. 1975, 1976a and b, Yan 1979, Dillon _et al_. 1979). These analyses are summarized in the following discussion.

Several investigators have demonstrated that a reduction in lake pH results in a reduction in the richness or in the diversity of phytoplankton communities, especially at pH levels <5.5 (Almer _et al_. 1974, Leivestad _et_ _al_. 1976, Kwiatkowski and Roff 1976). For the Sudbury lakes, taxa were identified to the generic not specific levels but the same trend was evident. The number of genera observed in Clearwater Lake varied from 7.5 to 10.1 per collection from 1973 to 1978 (range in monthly-weighted averages calculated over the ice-free season, Appendix 7). Lohi, Middle and Hannah Lakes, the 3 other acidified, Cu- and Ni-contaminated lakes, had similar numbers of 6.8, 6.0 and 8.5 genera per collection, respectively, prior to manipulation. A slightly higher average of 11.6 genera per collection occurred in Mountaintop Lake prior to fertilization, suggesting that some of the reduction in richness observed in the other acidic lakes may have been attributable to their contamination with the metals. Much higher numbers of 19.6, 18.3 and 21.5 genera per collection were observed, respectively, in Nelson Lake, stations 1 and 4 (pH 5.7) and in Labelle Lake (pH 6.0). Yan (1979) noted a similar average of 19.5 genera per collection in Blue Chalk Lake, a non-acidic lake in central Ontario.

While it was apparent that richness of genera was reduced in the acidic lakes, many algae are tolerant of acidic, metal-contaminated conditions. In 97 samples from Clearwater Lake, collected from 1973 to 1978, a total of 67 genera of algae were identified. There were representatives of all taxonomic classes (Appendix 7).

Softwater lakes in Ontario that are not enriched with nutrients are typically dominated by chrysophytes (Nicholls 1976, Schindler and Holmgren 1971) or by diatoms (Duthie and Ostrofsky 1974, Nicholls 1976a). In the Sudbury acidic lakes, dinoflagellates were the dominant taxa in terms of relative contribution to total biomass (Fig. 1-7). They formed virtually 100% of the biomass in Clearwater Lake on several occasions (Fig. 1-8). Dinoflagellates also usually replace chrysophytes in acidic lakes that are not contaminated with Cu and Ni (Almer _et al_. 1978, Yan and Stokes 1978), although at pH levels of ~5.0 such lakes may occasionally remain chrysophyte-dominated (Hendrey _et al_. 1980). It is not understood why dinoflagellates become dominant in the phytoplankton after acidification. They may be the dominant phytoplankters over a wide range of trophic conditions as well, including extremely oligotrophic lakes, such as Waldo Lake in Oregon (Malueg _et al_. 1972), and eutrophic lakes, such as Lake Kinneret in Israel (Berman and Rodhe 1971).

In Clearwater Lake the dominant species of dinoflagellate was _Peridinium inconspicuum_. This species is also the dominant dinoflagellate in acidic lakes in the La Cloche Mountains (Stokes unpub. data) and in Sweden (Hörnström _et al_. 1973).

The biomass averaged over the ice-free season of the phytoplankton of Clearwater Lake varied from 0.30 to 0.70 mg L^{-1} from 1973 to 1978. Considered together with data collected from Precambrian Shield lakes in central Ontario that were sampled in the same way as the Sudbury Lakes, the biomass of 8 lakes with pH >5.5 was not significantly different ($p > 0.05$, t-test of difference between means) from the biomass of the Sudbury lakes with pH <5.5 (Table 1-9), supporting previous suggestions (Almer _et al_. 1978, Yan 1979) that acidification will not result in a reduction in total biomass.

Information concerning the affects of acidification on phytoplankton productivity are very limited. In a recent review, Hendrey _et al_. (1980) concluded that acidification does not result in a reduction in productivity. No reductions in productivity have accompanied the experimental reduction in pH of Lake 223 in

Table 1-9: Phytoplankton biomass averaged over the ice-free season from the Sudbury lakes prior to any chemical manipulations. Biomass from six non-acidic oligotrophic lakes in Muskoka-Haliburton are presented for comparison (Nicholls unpub. data).

Lake		pH	TP (mg m^{-3})	Biomass (mg L^{-1})
Clearwater	1973	4.29	5.9	0.55
	1974	4.24	5.5	0.70
	1975	4.33	4.1	0.47
	1976	4.23	5.2	0.37
	1977	4.10	6.5	0.56
	1978	4.40	4.6	0.30
Swan	1977	3.96	10.9	2.14
Lohi	1973	4.39	6.1	0.65
Middle	1973	4.41		0.46
Hannah	1973	4.31	8.4	0.26
	1974	4.31	5.7	0.34
Nelson-1	1975	5.73	4.6	0.34
Joe	1975	5.57	4.8	0.38
Red Chalk	1976-1978	6.32	4.5	0.65
Blue Chalk	1977-1978	6.44	5.4	0.36
Harp	1977-1978	6.24	6.5	0.65
Jerry	1977-1978	6.28	8.3	1.06
Dickie	1976-1978	5.70	11.7	0.89
Chub	1976-1978	5.76	11.7	0.66

northwestern Ontario from 6.7 to 5.6. In fact Schindler (1980) observed an increase in productivity. Limited productivity data from Clearwater Lake have been previously compared with data from Blue Chalk Lake in central Ontario. No difference in productivity was observed (Dillon et al. 1979), but the data were not corrected for differences in total irradiance among days of measurement. One method of correcting the data is to convert the carbon uptake data to quantities of chemical energy stored by the plankters by assuming, as did Schindler and Nighswander (1970), that carbohydrate is only photosynthate (1gC = 11.25 kcal), then dividing by total surface irradiance to obtain an estimate of efficiency. Production efficiencies calculated in this way for Clearwater Lake were similar to those of Blue Chalk Lake and similar to efficiencies calculated by Tilzer et al.(1975) for Finstertaler See in Austria and Castle Lake in the U.S.A., two oligotrophic, subalpine lakes (Table 1-10). This comparison supports the previous conclusion that the productivity of the phytoplankton Clearwater Lake was not different from that of Blue Chalk Lake. As the original set of data was small, 6 measurements in Clearwater Lake and 7 measurements in Blue Chalk Lake, the conclusions should be regarded as tentative.

In lakes with similar hypolimnetic temperatures and morphometry, areal hypolimnetic oxygen depletion rates (AHOD) are usually well correlated with and are often considered to be a rough measure of productivity (Cornett and Rigler 1979). The AHOD's for Clearwater Lake could not be calculated in 1973 and 1974, because many hypolimnetic temperature data were missing, and in 1976, because photosynthesis within the hypolimnion often increased the total mass of hypolimnetic oxygen. The AHOD was 0.013 mg O_2 cm^{-2} day^{-1} (0.009-0.022) on average in 1975 and 1977 to 1979,

Table 1-10: Efficiencies of phytoplankton productivity in Clearwater and Blue Chalk Lakes in 1976. Range of efficiencies in ultra-oligotrophic to eutrophic lakes are included for comparison. Lakes are listed in order of increasing eutrophy as indicated by phytoplankton biomass.

Lake	Phytoplankton Biomass ($mg\ L^{-1}$)	Efficiency[1] (%)
Tahoe[2], U.S.A.	0.083	0.035
Blue Chalk, Ontario	0.33	0.051
Clearwater, Ontario	0.37	0.060
Castle[2], U.S.A.	0.44	0.040
Finstertaler[2], Austria	0.52	0.068
Wingra[2], U.S.A.	7.4	0.45
Leven[2], Scotland	14.8	1.76

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[1] Efficiency was calculated as productivity ($mg\ C\ m^{-2}\ day^{-1}$) converted to energy units assuming 1gC = 11.25 kcal, divided by surface light for the day

[2] from Tilzer *et al.* (1975)

and was at the bottom end of the range of 0.013-0.038 mg O_2 cm^{-2} day^{-1} indicated by Lasenby (1975) to be typical of non-acidic oligotrophic lakes in Haliburton, Ontario. Comparisons with these non-acidic lakes are complex, however, as hypolimnetic temperatures were warmer in Clearwater Lake than in non-acidic oligotrophic lakes of similar depth (perhaps increasing the AHOD), while the hypolimnion was within the trophogenic zone of the lake (perhaps decreasing the AHOD).

ii. Macrophytes

The macrophytes of six of the SES lakes were surveyed during 1977 and 1978 (Table 1-11). Information collected included presence, abundance and, in the case of Clearwater Lake, biomass of species, and the distribution of trace metals between water, sediment and plants. The chemical and biological data discussed in this section all arise from a larger study of 46 Ontario lakes which will be published elsewhere. Trace metal concentrations in macrophytes in Harp and Red Chalk Lakes, two non-acidic lakes in south-central Ontario, were measured as part of this larger study.

a. Species Composition and Abundance

Generally, the macrophyte vegetation of the SES lakes was similar in structure to the vegetation of 24 clear and coloured, low alkalinity lakes in south-central Ontario. Dense, low-statured mats of isoetid forms predominated. Most vegetation was found between 0 and 3 m depths, but higher plants occasionally grew at 5 m and mosses as deep as 8 m.

No consistent pattern of specific cover dominance occurred in the vegetation of these lakes. *Eriocaulon septangulare* dominated in two lakes, *Eleocharis acicularis* in two others and, in the final two, dominance was shared between these two species and *Myriophyllum tenellum*.

Table I-11: Vascular macrophyte species[1] present in six Sudbury lakes.

Species	Middle	Clearwater	Lohi	Hannah	Nelson	LaBelle
Eriocaulon septangulare With.	+	+	+	+	+	+
Eleocharis acicularis R.&.S.	+	+	+	+	+	
Juncus pelocarpus Mey.	+	+	+	+	+	
Sagitteria spp.	+		+	+	+	
Myriophyllum tenellum Bigel.		+	+		+	
Utricularia vulgaris L.		+	+			
U. cornuta Michx.			+			+
Isoetes spp.				+	+	
Lobelia dortmanna L.					+	+
Lycopus sp.		+				
Eleocharis robbinsii Oakes			+			
Utricularia resupinata B.D. Greene				+		
Pontederia chordata L.				+		
Juncus militaris Bigel					+	
Myriophyllum farwellii Morong.						+
Nitella sp.						+
Potamogeton natans L.						+
Scirpus subterminalis Torr.						+
Σ Species	4	6	8	7	8	7

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[1] Mosses present were *Drepanocladus exannulatus* (BSG) Warnst. and *Mnium drummondii* Bruch & Schimp. in *Clearwater Lake*, *Fontinalis dalecarlica* BSG in Nelson Lake and *Fontinalis* sp. in Lohi Lake.

Between 5 and 28 (mean of 17) species (excluding mosses) occurred in each of 24 south-central Ontario lakes. The floras of the Sudbury lakes were impoverished by comparison (Table 1-11), perhaps because of metal contamination (Gorham and Gordon 1963, Miller _et_ _al_. in prep.).

The frequency of occurrence of species within the Sudbury lakes is compared to the average occurrence of the same species in the 24 south-central Ontario lakes in Table 1-12. _Eleocharis_ _acicularis_, _Eriocaulon_ _septangulare_, _Juncus_ _pelocarpus_ and _Myriophyllum_ _tenellum_ were as common in the Sudbury lakes as they were in the other lakes. The first species is known to tolerate acidified, metal-contaminated conditions (Ehrle 1960). It appears that the latter three species also fall into this category.

Contrary to observations made in Swedish acidic lakes (Grahn _et_ _al_. 1974, Grahn 1977), extensive beds of _Sphagnum_ were not observed in the study lakes; however, other moss species were a significant part of the vegetation in Lohi and Clearwater Lakes.

b. _Biomass_

In Clearwater Lake plant biomass was measured on a monthly basis from May to October 1978. The seasonal average biomass of macrophytes in the lake was 510 ± 98 g m^{-2} calculated per unit area of vegetated zone. The maximum biomass observed in one sample was 930 g m^{-2}.

An average vegetated zone biomass of 510 g m^{-2} is exceptionally high for an oligotrophic lake in North America. Harp and Red Chalk Lakes had 107 ± 27 and 72 ± 11 g m^{-2}, respectively, of macrophyte biomass (Miller _et_ _al_. in prep.). Moeller (1975) measured 7.1 g m^{-2} for an isoetid dominated lake the U.S.A. However, the oligotrophic Danish Lake Kalgaard had an ash-free dry weight of

Table 1-12: A comparison of the percent occurrence of macrophyte species of the six Sudbury lakes and the 24 south-central Ontario lakes. Only species with an occurrence of >50% in the latter lakes were included.

Species	Percent Occurrence 24 south-central Ontario lakes	6 Sudbury lakes
Brasenia schreberi Gmel.	58	0
Eleocharis acicularis R. & S.	83	83
Eriocaulon septangulare With.	96	100
Isoetes spp.	83	33
Juncus militaris Bigel.	54	0
Juncus pelocarpus Mey.	67	83
Lobelia dortmanna L.	79	33
Myriophyllum tenellum Bigel.	58	50
Nuphar variegatum Engelm.	83	0
Nymphea odorata Ait.	67	0
Pontederia chordata L.	92	16
Potamogeton epihydrus Raf.	75	0
Sparganium spp.	79	0
Utricularia purpurea Walt.	58	0
U. resupinata B.D. Greene	71	16
U. vulgaris L.	71	33

107 g m^{-2}, equivalent to a dry weight of 130 g m^{-2} (Sand-Jenson and Sondergaard 1979). The average biomass in Clearwater Lake was about half that observed in Chemung Lake, a very productive lake in southern Ontario (Wile and Hitchin 1977), but the greatest biomass observed in a single quadrat exceeded that of Chemung Lake.

The seasonal distribution of biomass in Clearwater Lake is typical of an evergreen isoetid community. Seasonal changes in biomass were small enough with respect to the sample variation that they remained undetected in an analysis of the variance of monthly samples. This contrasts sharply with the vegetation of Chemung Lake which is dominated by vittate forms and shows a distinct seasonality (Wile and Hitchin 1977).

c. Metal Accumulation

Concentrations of Ni, Cu, Zn, Pb, Cd and Mn in the tissues of *Eriocaulon septangulare* taken from sites in Clearwater Lake were significantly higher than those in the adjacent littoral sediments (Miller *et al.* in press). This was similar to the pattern of accumulation found in this plant at sites in Harp and Red Chalk Lakes, two non-acidic lakes in central Ontario. However, plant tissue levels of Ni and Cu were much higher in Clearwater Lake than in the Harp or Red Chalk Lake samples, no doubt reflecting the elevated sediment levels. Conversely, Zn levels were lower in plant tissue from Clearwater Lake despite the same sediment Zn concentrations in all three lakes.

Miller *et al.* (in press) have found that over a large number of Ontario lakes the concentration of Zn in *Eriocaulon septangulare* tissue tends to decrease with increasing Cu/Ni contamination of the sediments. They suggest that there may be a competitive relationship between Cu and Zn for uptake sites within the plant.

By applying the concentration measured in the tissue of *Eriocaulon* in Clearwater Lake to the mean total plant biomass, estimates of the total mass of each metal present in the vegetation were derived. The vegetation of Clearwater Lake contained an estimated 12.1 kg of Cu, 8.2 kg of Ni, 4.3 kg of Mn, 2.6 kg of Pb, 1.0 kg of Zn, 457 kg of Fe, 0.05 kg of Cd and 142 kg of Al. With the exception of Fe, these amounts are very small when compared with the total mass of each metal in the lake excluding the sediments. The mass of copper found in the vegetation for example, was <2% of that in the water column in 1978.

E. Zooplankton

i. Crustacea

Acidification results in reductions in the diversity of zooplankton communities as it does in phytoplankton communities (Sprules 1975, Roff and Kwiatkowski 1977, Fryer 1980). Species richness in the acid- and metal-contaminated SES lakes was reduced. The average number of species of planktonic crustacea observed per collection was 3-4 times less than in morphometrically-similar, oligotrophic, non-acidic lakes in Muskoka-Haliburton (Fig. 1-9).

Acidified lakes in the La Cloche Mountains are not heavily contaminated with Cu and Ni. Levels of each metal are usually <10 $\mu g\ L^{-1}$. In these lakes and in other acidic lakes >50 km from Sudbury, *Diaptomus minutus* is usually the dominant zooplankter. *Bosmina longirostris*, *Holopedium gibberum* and *Diaphanosoma leuchtenbergianum* are often co-dominant. While they occur, species of *Daphnia* are reduced in importance. The dominant cyclopoid copepods are *Cyclops bicuspidatus thomasi* and *Mesocyclops edax* (Sprules 1975, Roff and Kwiatkowski 1977, Keller 1981). The composition of the crustacean zooplankton community of the acidic

SES lakes differed from this typical pattern (Yan and Strus 1980). In Clearwater Lake, and in the other acidic lakes, *Cyclops vernalis* was the common cyclopoid rather than, *C. bicuspidatus thomasi* or *M. edax*. Seasonal distribution of *C. vernalis* was unimodal in Clearwater Lake in all years except 1975 (Fig. 1-10). *D. minutus* was rare or absent and *H. gibberum* and *D. leuchtenbergianum* were absent (Table 1-13). Clearwater Lake is morphometrically similar to the acidic La Cloche Mountain Lakes. The lakes are in the same faunistic region with respect to zooplankton (Patalas 1971), have no fish and have similar phytoplankton biomass and community assemblages (Yan and Strus 1980). Therefore, the most probable explanation for the difference in zooplankton community structure is the presence of metals in the Sudbury lakes at potentially toxic concentrations. Levels of Cu and Ni in Clearwater Lake, for example, exceed the 16% reproductive impairment concentrations for *Daphnia magna* reported by Biesinger and Christensen (1972).

B. longirostris was the dominant zooplankter in all of the acidic study lakes forming 78-95% of the ice-free period average crustacean biomass in Clearwater Lake, for example, between 1973 and 1978. In Nelson Lake, in contrast, it formed only 3% of the biomass (Table 1-13), a pattern that is more typical of non-acidic lakes in Ontario (Yan and Strus 1980). The magnitude and timing of population maxima of *B. longirostris* in Clearwater Lake varied substantially among years (Fig. 1-11).

The biomass of the zooplankton community of non-acidic lakes in Muskoka-Haliburton is typically 26-87 mg m^{-3} when averaged over the ice free season. (Table 1-13). The biomass of Nelson Lake was within this range, but that of the acidic lakes was generally much lower (Table 1-13), because of the small size of the community

Table 1-13: Percentage contribution of species to biomass of crustacean zooplankton, averaged over the ice-free season. Total biomass is indicated. Species contributing <1% to the total are not included but may be found in Appendix 8.

	Clearwater 1973-1978[1]	Lohi 1973[2]	Middle 1973[2]	Hannah 1973-1974[3]	Nelson Station 1 1975[2]
Total Biomass (mg m^{-3})	4.3-13.8	24.0	13.7	0.70	34.0
Bosmina longirostris	78-95	81	92	47	2.8
Chydorus sphaericus	0-1.0	0.5	0.4	9.2	<0.1
Daphnia longiremis	-	-	-	-	1.2
Simocephalus serrulatus	0-1.1	-	-	-	-
Cyclops scutifer	-	-	-	-	5.1
C. vernalis	0-3.9	2.7	0.3	15	0.3
Mesocyclops edax	-	-	-	-	10
cyclopoid copepodid	0.5-7.5	2.9	0.8	3.4	15
Diaptomus minutus	0-0.1	-	-	-	22
Epischura lacustris	0-<0.1	-	-	1.7	-
calanoid copepodid	0-0.2	-	-	10	18
nauplii	<0.1-13	13	6.3	13	25

[1] range of averages for ice-free season

[2] prior to addition of base

[3] average of 1973 and 1974 data

dominant, B. longirostris, and with the exception of Lohi Lake, because of reduced population densities. The lowest biomass (<1 mg m^{-3}) was observed in Hannah Lake, the lake with the highest levels of metals (Table 1-5). This was probably attributable to metal toxicity.

Zooplankton community biomass varied greatly over the season in Clearwater Lake and in the other acidic SES lakes. For other acidic lakes, only the studies of Bible (1972), who compared zooplankton in the main basin of Cheat Lake with that of two less acidic backwaters, and Roff and Kwiatkowski (1977), who studied 6 lakes in the La Cloche Mountains ranging in pH from 4 to 7, included sufficient samples to assess whether standing stocks of zooplankton are reduced by acidification. While the former study was of an acid mine drainage (AMD) lake with unknown levels of metals, and the latter study included data from only 2 months in each of 2 years, they suggest that biomass was reduced, as in Clearwater Lake.

The feeding rate of filter feeding zooplankton is a product of the concentration of edible food (up to saturating food concentrations) and the filtering rate of the individual zooplankton. Filtering rates of individual zooplankton on phytoplankton are influenced by a variety of factors including size, shape, taxonomic affinity and outer envelope of the prey (McNaught et al. 1980). Rates are independent of food concentration up to specific thresholds beyond which they decrease (Rigler 1961). Despite this complexity, filtering rates of zooplankton communities are empirically correlated with the size of the filter-feeders and their density, the product of which is community biomass. As zooplankton community biomass was reduced in the acidic SES lakes while phytoplankton productivity was not reduced (Table 1-10), Yan and Strus (1980) suggested that the efficiency of energy transfer from primary to secondary trophic levels should be lower in Clearwater Lake than in non-acidic oligotrophic lakes. Because of the lower filtering rates, they suggested that the domination of the phytoplankton community of Clearwater Lake by dinoflagellates was not due to selective grazing.

ii. Rotatoria

There is some evidence to suggest that certain species of rotifers may be more tolerant of acidic conditions than crustacean zooplankters. Stockinger and Hays (1960) noted that *Keratella* was very abundant in a strip mine pond of pH 3.2 - 3.6 in Kansas. *Brachionus urceolaris* formed 98% of the zooplankton biomass in a pond of pH 3.0 to 3.4 in Indiana (Smith and Frey 1971) and virtually all of the biomass in an AMD pond of pH 3.4 to 4.6 in Missouri (Campbell *et al*. 1964). In contrast, Almer *et al*. (1974) indicated that rotifer diversities were reduced in Sweden, as were crustacean diversities, and Roff and Kwiatkowski (1977) indicated that rotifer abundances were lowest in their two most acidic study lakes.

In the Muskoka-Haliburton lakes and in Nelson Lake, rotifers formed a very small fraction of the total biomass (usually 1% or less, Table 1-14). They formed a larger fraction of the biomass in Lakes 122 and 132 in northwestern Ontario and in Mirror Lake in New Hampshire (Table 1-14); however, weights used to convert rotifer abundances to biomasses were much higher in these two studies than in our study lakes, suggesting that the differences in relative contributions of rotifers to total zooplankton biomass might be an artifact of data treatment (Table 1-15).

Table 1-14: Relative contribution of rotifers, cladocerans and copepods to zooplankton biomass in SES and other soft-water oligotrophic lakes.

Lake		Total Biomass (mg m^{-3})	% Biomass			Source
			Copepoda	Cladocera	Rotifera	
Clearwater	1976	12.9	12	55	33	This study
	1977	16.5	5	79	16	" "
	1978	7.5	14	53	33	" "
Nelson	1975	34.1	96	4	<1	Yan *et al.* (1977)
	1976	36.1	82	16	3	"
Chub	1977	49.0	74	25	1	Yan and Strus (1980) and Yan (unpub. data)
Dickie	"	86.6	35	64	1	
Harp	"	31.9	44	55	1	"
Jerry	"	26.2	79	20	1	"
Blue Chalk	"	49.0	69	31	<1	"
Red Chalk	"	31.1	64	36	<1	"
Clear		145	38	60	2	Schindler and Noven (1971)
ELA 122		81	61	28	12	"
ELA 132		169	34	58	12	"
Chester Morse		20.7	53	46	1	Pederson *et al.* (1975)
Findley		25.4	59	40	1	"
Mirror		-	55	28	16	Makarewicz and Likens (1979)
Maggiore (Bay of Ispra)		30.0	68	22	10	Ravera (1969)

Table 1-15: Weights (µg animal^{-1}) used in three different studies to convert rotifer abundances to biomass.

	Makarewicz and Likens (1979)	Schindler and Noven (1971)	This Study
Kellicotia bostoniensis	0.066	0.045	0.009[1]
K. longispina	0.100	0.090	0.016[1]
Keratella cochlearis	0.070	0.035	0.010[1]
K. taurocephala	0.096	0.060	0.020[2]
Polyarthra vulgaris	0.060	0.070	0.034[1]
Trichocerca cylindrica		0.005	0.071[1]

[1] from Lawrence *et al.* (in preparation)
[2] determined from Clearwater collections

From 1976 to 1978, 14 species of rotifers were identified in Clearwater Lake. As in the acidic La Cloche Mountain Lakes surveyed by Roff and Kwiatkowski (1977), the dominant species was Keratella taurocephala, which formed 91, 98 and 95% of the density of rotifers in 1976, 1977 and 1978, respectively (Table 1-16). Rotifers were much more important contributors to total biomass in Clearwater Lake than in non-acidic oligotrophic lakes (Table 1-14). Because they have shorter generation times than crustaceans, their contribution to the productivity of all zooplankton is undoubtedly even greater than their contribution to biomass (Makarawicz and Likens 1979).

Haney (1973) measured a filtering rate (the effective volume of water cleared of prey per unit time) of 0.44 mL (0.009 - 0.90) animal^{-1} day^{-1} for B. longirostris, the dominant crustacean zooplankter in Clearwater Lake with densities of 10-20 animals L^{-1}. He also measured filtering rates for Kellicottia of 0.007 mL animal^{-1} day^{-1}, about 60 times less than the average rate measured for B. longirostris. Edmondson (1965) indicated that Kellicottia and Keratella feed in much the same way on similar sized prey. As the two rotifers are of similar size, the filtering rates of Keratella are probably similar to that of Kellicottia. Thus, while K. taurocephala outnumbers B. longirostris by an order of magnitude on average in Clearwater Lake, the cladoceran is probably still the dominant grazer in the lake.

Table 1-16: Contributions of species to mean density of rotifers in the ice-free period in Clearwater Lake.

	% Density[1] 1976	1977	1978
Gastropus stylifer	7.7	<0.1	-
Keratella cochlearis	0.4	0.5	2.6
K. hiemalis	0.2	<0.1	-
K. taurocephala	90.7	98.0	95.0
Synchaeta sp.	0.5	<0.1	1.4
Trichocera multicrinis	0.3	1.3	0.8
Total Density (animals L^{-1})	198	131	105

[1] also present but forming <0.1% of ice-free period density were *Kellicotia bostoniensis*, *K. longispina*, *Keratella quadrata*, *Monostyla lunaris*, *Lecane* sp., *Polyarthra vulgaris*, *P. euryptera*, *Synchaeta pectinata*, *Trichocerca cylindrica* and an unidentified species.

F. Summary

1. From 1973 to 1979, Clearwater Lake, near Sudbury, Ontario, was intensively monitored as a reference for manipulation experiments performed on 6 other Sudbury-area lakes (Middle, Hannah, Lohi, Nelson, Mountaintop and Labelle Lakes), and to provide information on long-term variability of the chemistry and biota of an acidic lake. Clearwater, Lohi, Middle, Hannah and Mountaintop Lakes were all acidic lakes ($pH < 4.6$) with no fish populations, prior to manipulations. Labelle and Nelson Lakes were much less acidic ($pH = 6.0$ and 5.8, respectively) and supported fish populations.
2. Average concentrations of Cu, Ni, Zn, Al and Mn in Clearwater Lake in 1977 were 81,280,39,380 and 290 $\mu g\ L^{-1}$, respectively. Trace metal concentrations decreased in the 6 other lakes with increasing distance from Sudbury, but even at Mountaintop Lake, 50 km from the city, levels of Zn, Cu and Ni were well above background levels or levels in south-central Ontario lakes that are near no industrial centres but are receiving acidic precipitation.
3. Levels of major cations were much higher in Clearwater Lake than in south-central Ontario lakes, and decreased in lakes at increasing distance from Sudbury. Replacement of HCO_3^- by SO_4^{2-} as the dominant anion in Clearwater Lake indicated that acidification of the lake was probably attributable to the deposition of acidic sulphates.
4. Clearwater Lake was exceptionally clear. In consequence, the lake had a much thicker epilimnion, a warmer hypolimnion, and fall overturn occurred 4 to 8 weeks earlier than in a non-acidic, oligotrophic lake of similar morphometry and

fetch. As the entire lake was included in the trophogenic zone, depression of NO_3^- levels to below detection limits in the hypolimnion was probably attributable to photosynthetic activity in the profundal waters.

5. Biomass and productivity of the phytoplankton community of Clearwater Lake were not reduced by the low pH. Phytoplankton community diversity, estimated by richness of genera, was reduced and community structure was altered. Dinoflagellates, especially *Peridinium inconspicuum*, replaced the chrysophytes or diatoms that typically are dominant in non-acidic lakes.

6. *Eriocaulon septangulare*, *Eleocharis acicularis* and *Myriophyllum tenellum* dominated the macrophyte communities. The communities were similar in structure (dominated by isoetids forms), but impoverished in species in comparison to 24 lakes in south-central Ontario. Macrophyte standing stock was much higher in Clearwater Lake than in 2 non-acidic, oligotrophic lakes in south-central Ontario; in fact, it was as high as that observed in eutrophic Chemung Lake in southern Ontario. Dense beds of *Sphagnum*, similar to those reported in acidic Scandanavian lakes, were not observed in Sudbury lakes.

7. Zooplankton communities were apparently influenced by both the low pH and the high levels of metals in the acidic study lakes. Species richness was 3-4 times lower than in non-acidic lakes. *Bosmina longirostris* was the dominant crustacean zooplankter, forming 78-95% of the average crustacean biomass in Clearwater Lake. In contrast with phytoplankton, zooplankton standing stocks were reduced,

because of low densities and smaller size of the community dominants. Rotifers, especially *Keratella taurocephala*, were much more important components of the zooplankton in Clearwater Lake than in non-acidic lakes.

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Fig. 1-7. Relative contribution of Dinophyceae or Chrysophyceae plus Bacillariophyceae to total biomass averaged over the ice-free season vs. pH. Data are 1976-1978 averages from 6 Muskoka-Haliburton Lakes (■), (Nicholls in preparation) and premanipulation data from the SES Lakes Lohi (x), Middle (Δ), Hannah (▲), Clearwater (●), Nelson station 1 (o) and station 4 (◇), Joe (□) and Swan (◆).

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Fig. 1-11. Seasonal changes in the abundance of *Bosmina longirostris* in Clearwater Lake from 1973 to 1978.

Fig.1-1

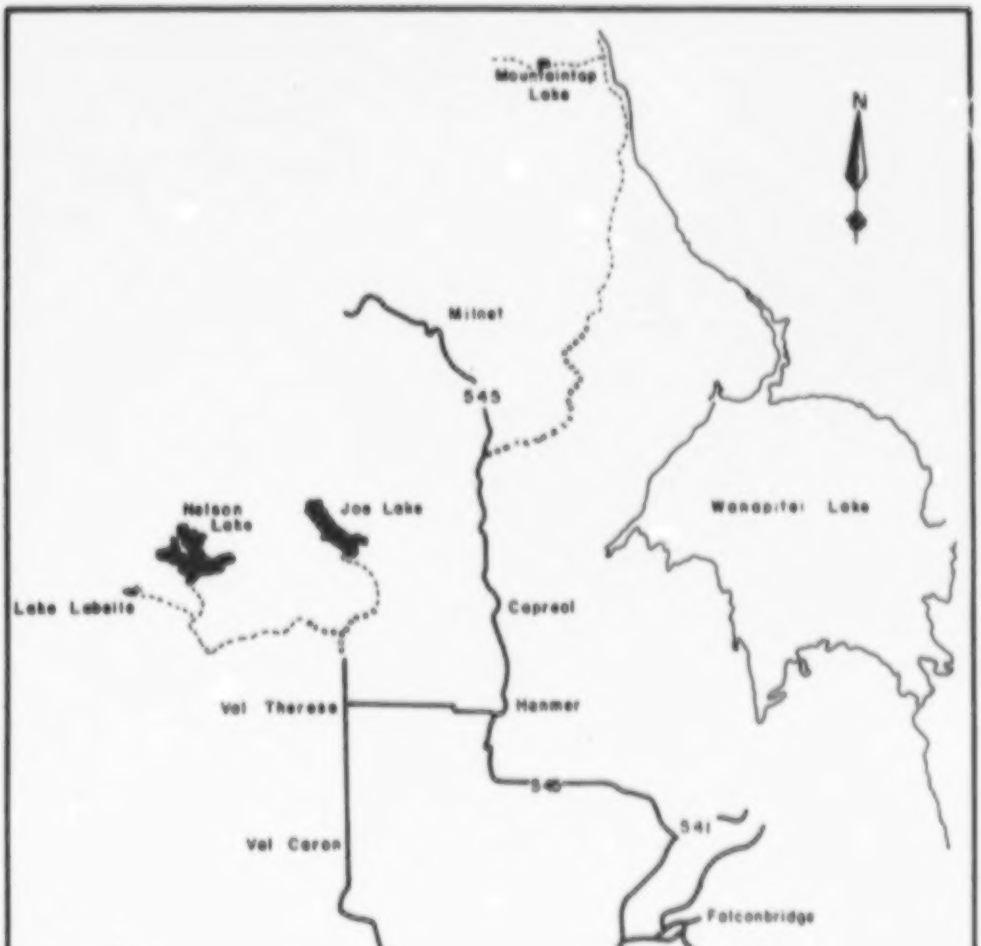

Mountaintop Lake
N
Milnet
545
Wanapitei Lake
Nelson Lake
Joe Lake
Lake Labelle
Capreol
Val Therese
Hanmer
545
541
Val Caron
Falconbridge
69
Garson Mine
144
46° 30′
17
Coniston
SUDBURY
Copper Cliff
Hannah Lake
69
0 Km
10 Km
17
Middle Lake
Lohi Lake
Swan Lake
Clearwater Lake
69
81° 00′

Fig.1-2

CLEARWATER LAKE

Isotherm (°C) maps

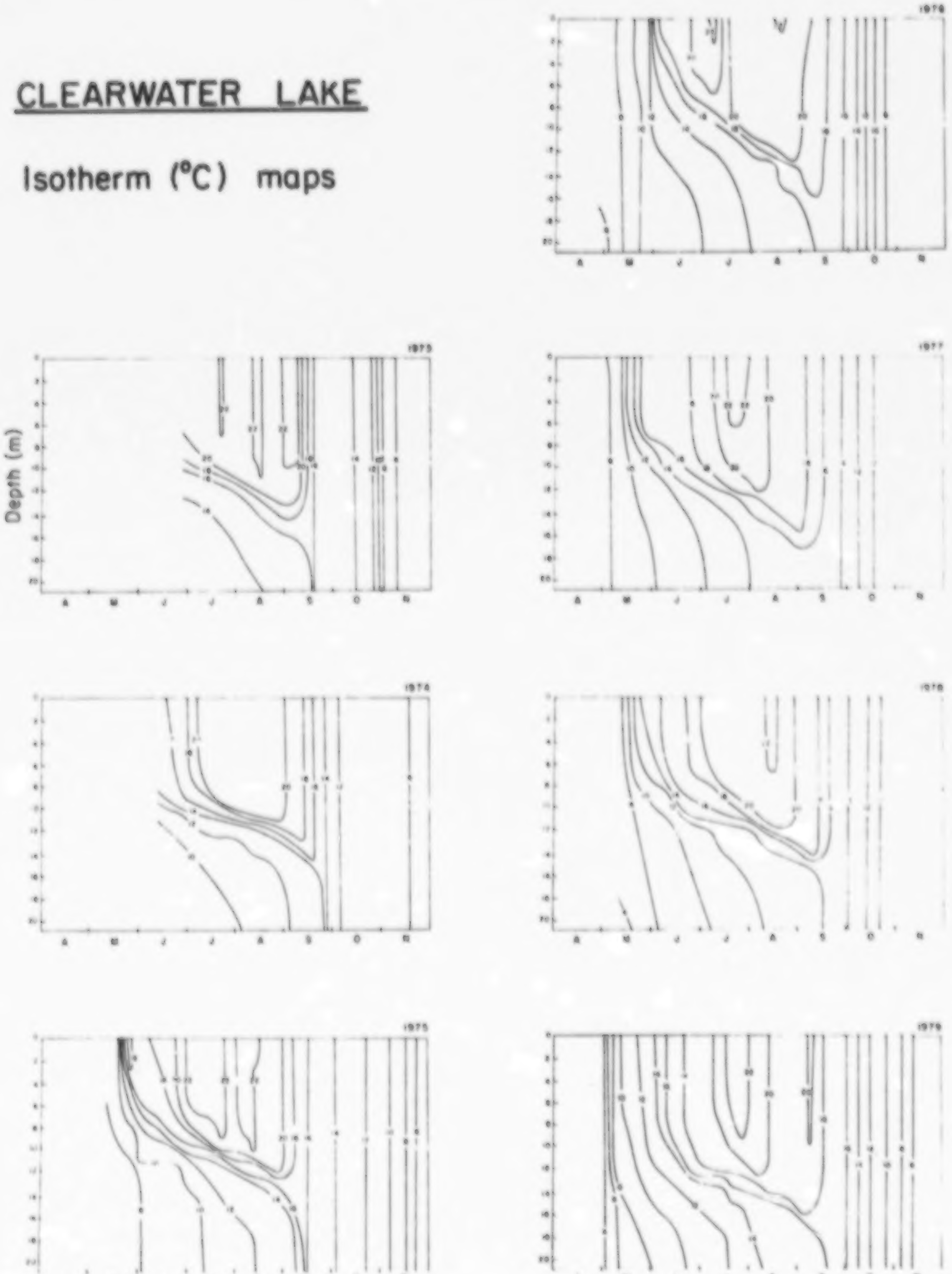


Fig. 1-3

CLEARWATER LAKE

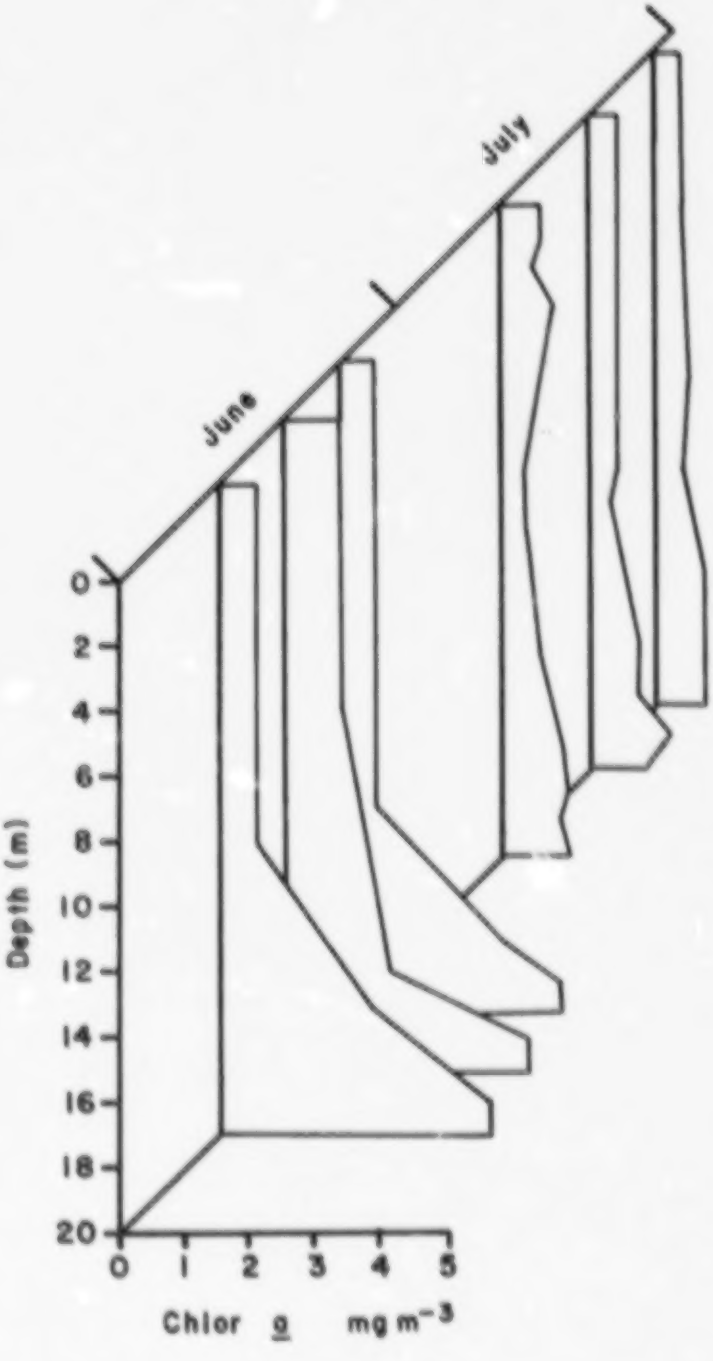
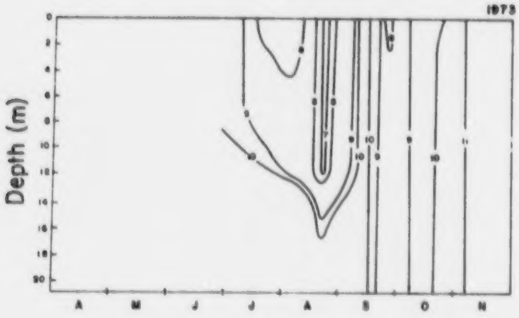
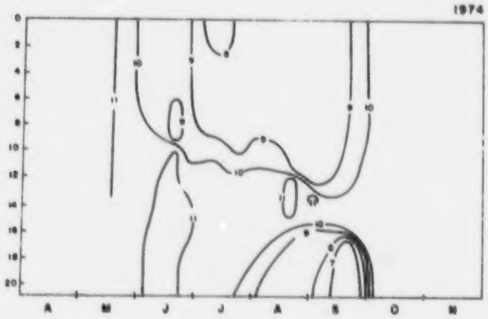


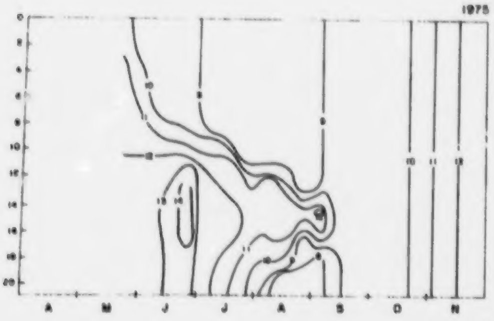
Fig. 1-4

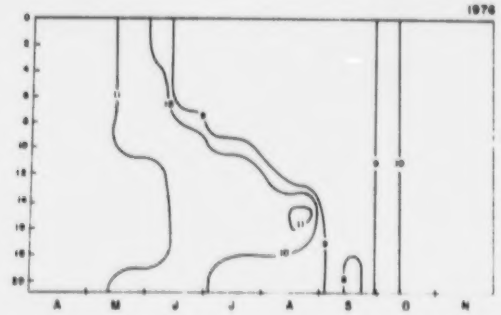
CLEARWATER LAKE

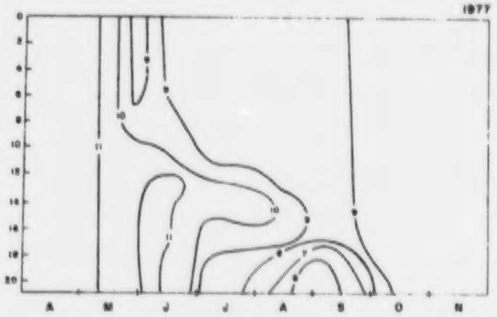
Oxygen (mg L⁻¹) isopleth maps

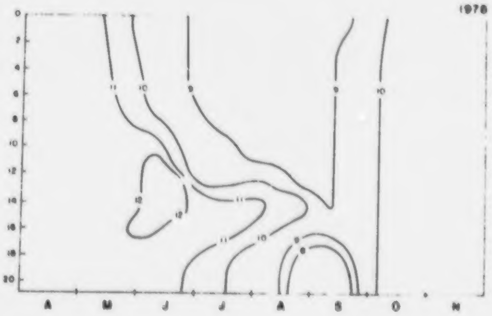












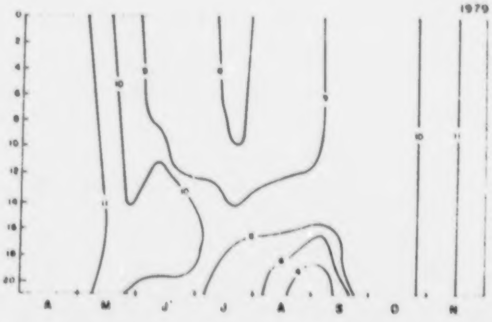
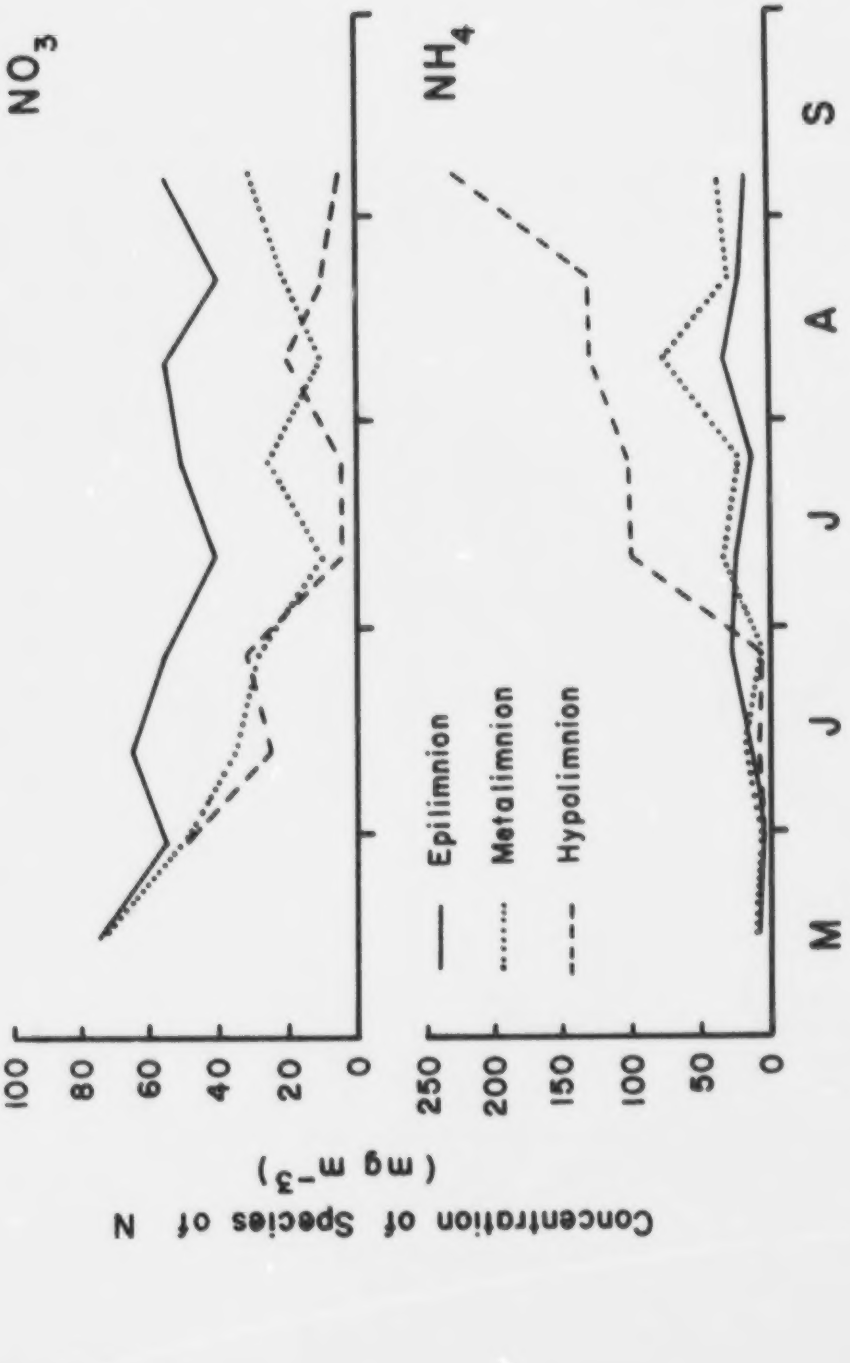
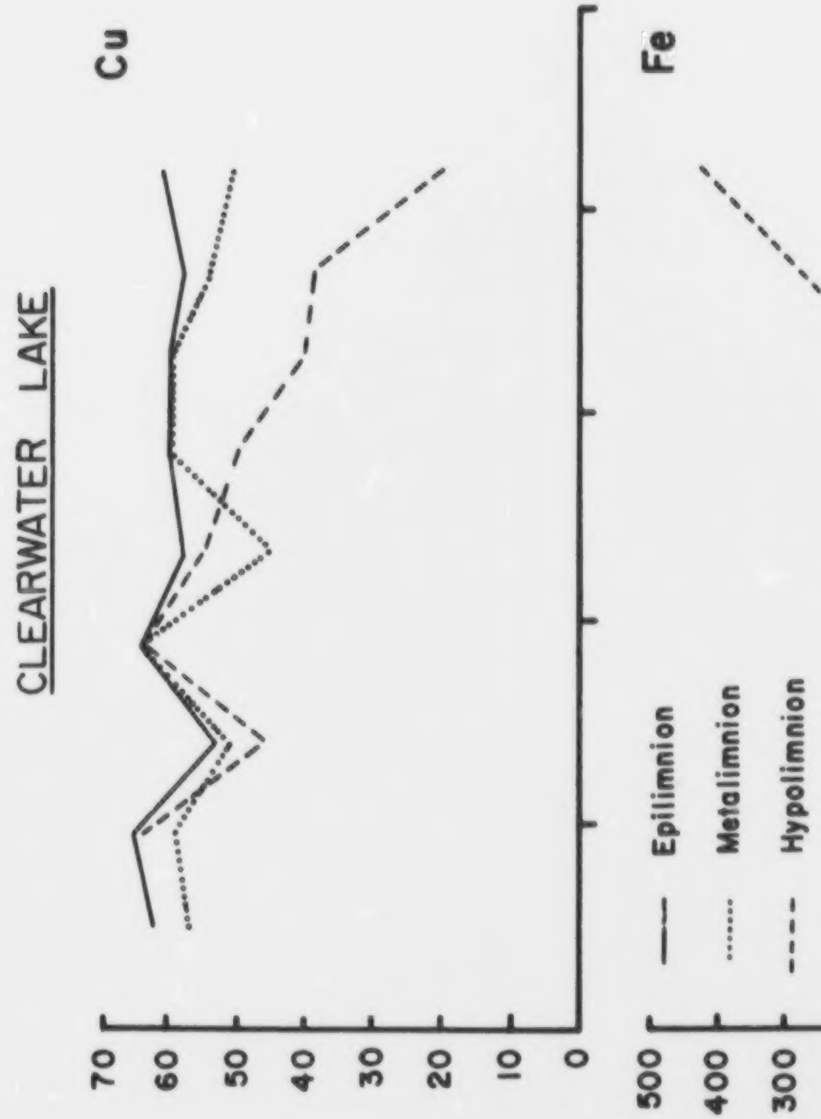


Fig.1-5



CLEARWATER LAKE

Fig. 1-6



CLEARWATER LAKE
Cu
Fe
Concentration of Metal
(mg m⁻³)
70
60
50
40
30
20
10
0
500
400
300
200
100
0
M
J
J
A
S
Epilimnion
Metalimnion
Hypolimnion

Fig.1-7

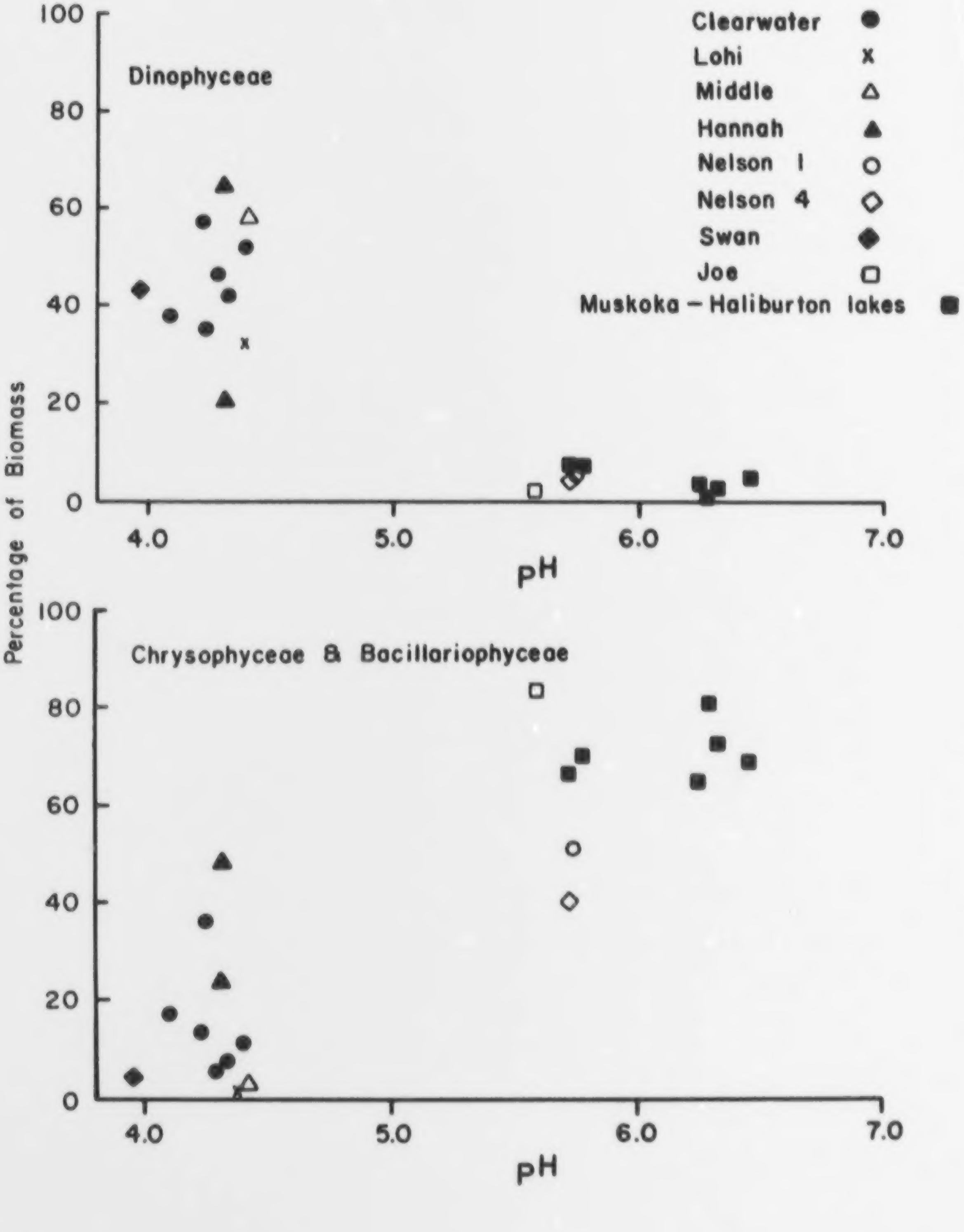

Dinophyceae
Clearwater ●
Lohi x
Middle △
Hannah ▲
Nelson 1 ○
Nelson 4 ◇
Swan ◆
Joe □
Muskoka — Haliburton lakes ■
Percentage of Biomass
100
80
60
40
20
0
4.0
5.0
6.0
7.0
pH
Chrysophyceae & Bacillariophyceae
100
80
60
40
20
0
4.0
5.0
6.0
7.0
pH

Fig. 1-B

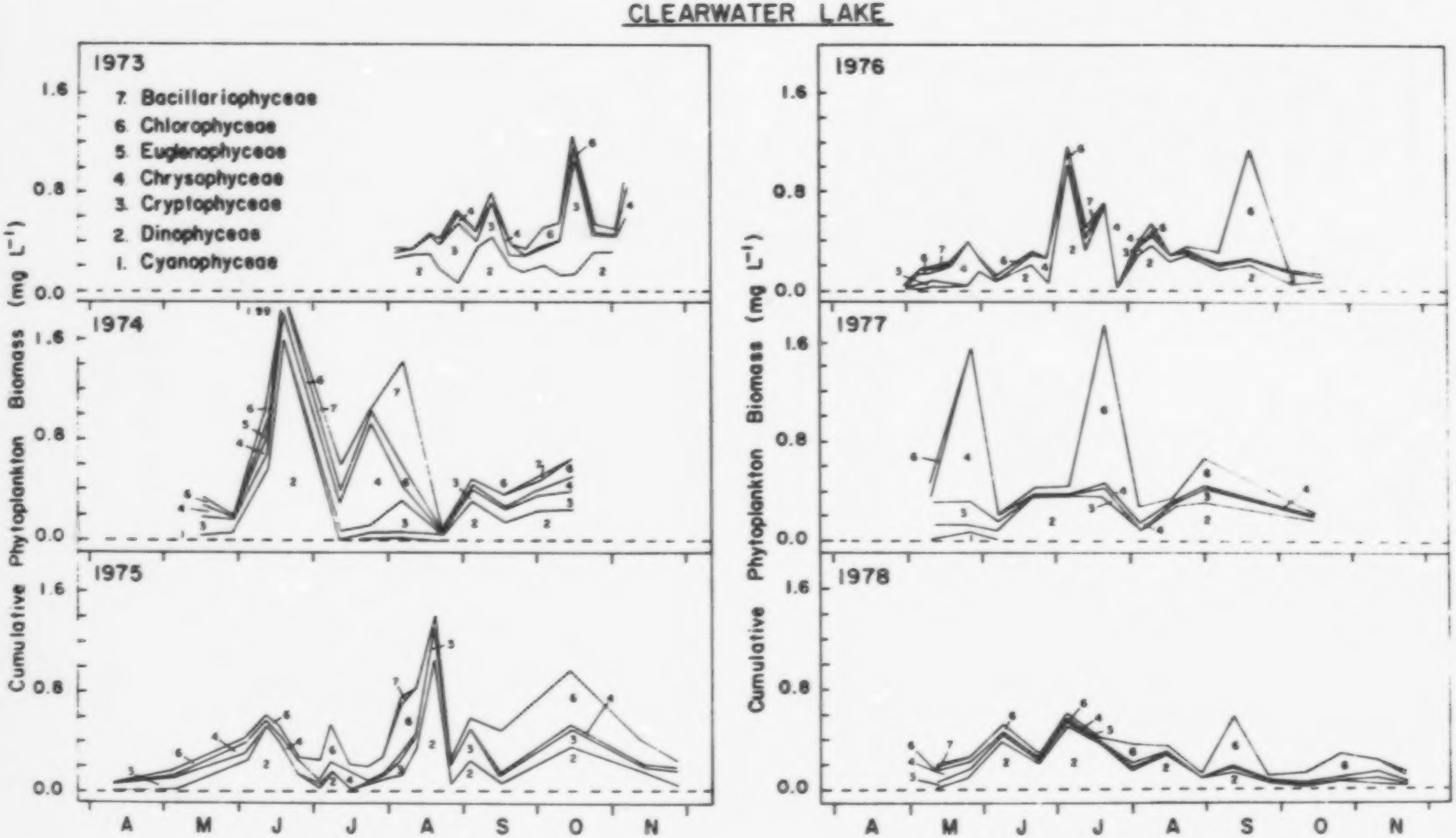
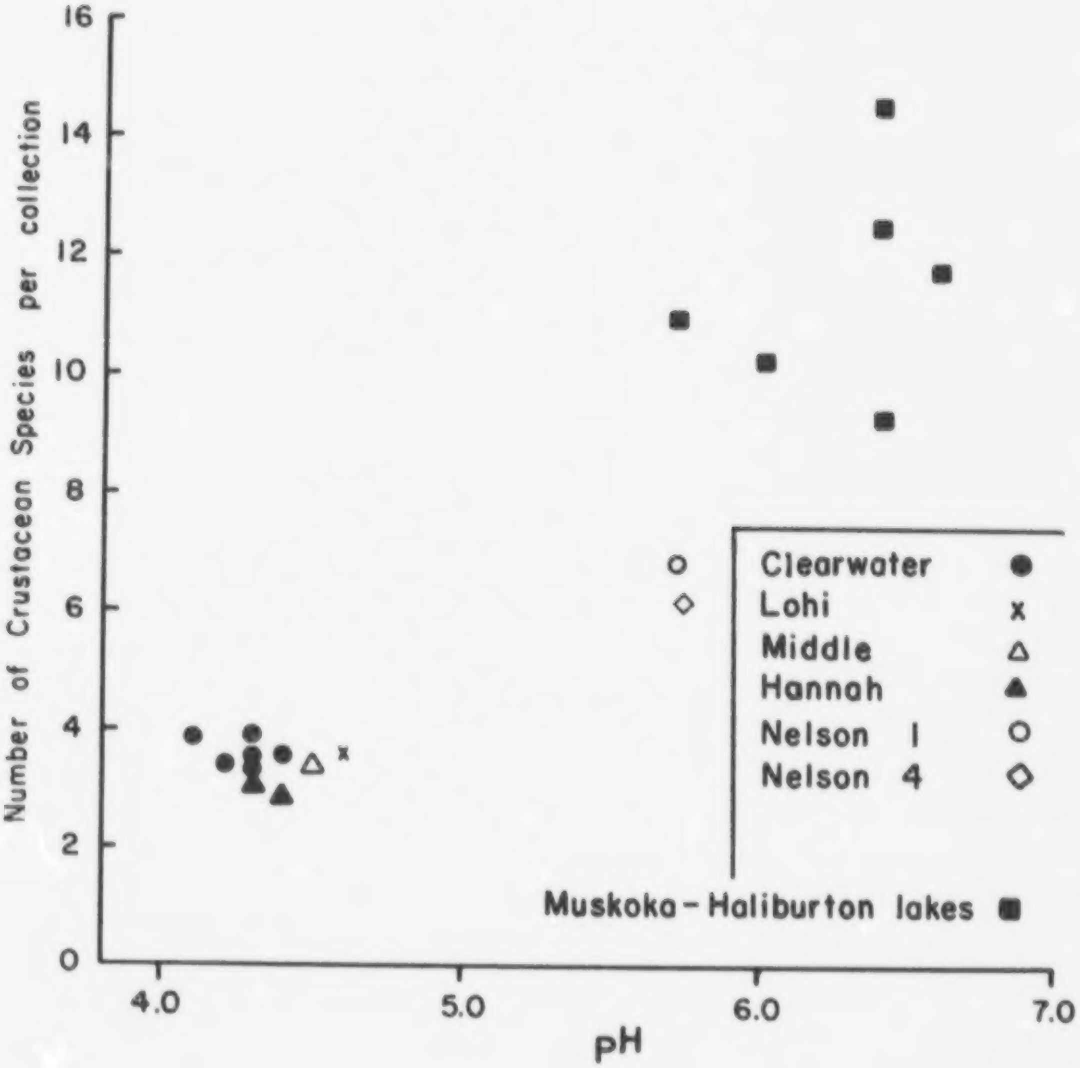

CLEARWATER LAKE

Fig.1-9



Number of Crustacean Species per collection
0
2
4
6
8
10
12
14
16
4.0
5.0
6.0
7.0
pH
Clearwater ●
Lohi x
Middle △
Hannah ▲
Nelson 1 ○
Nelson 4 ◇
Muskoka-Haliburton lakes ■

CLEARWATER LAKE

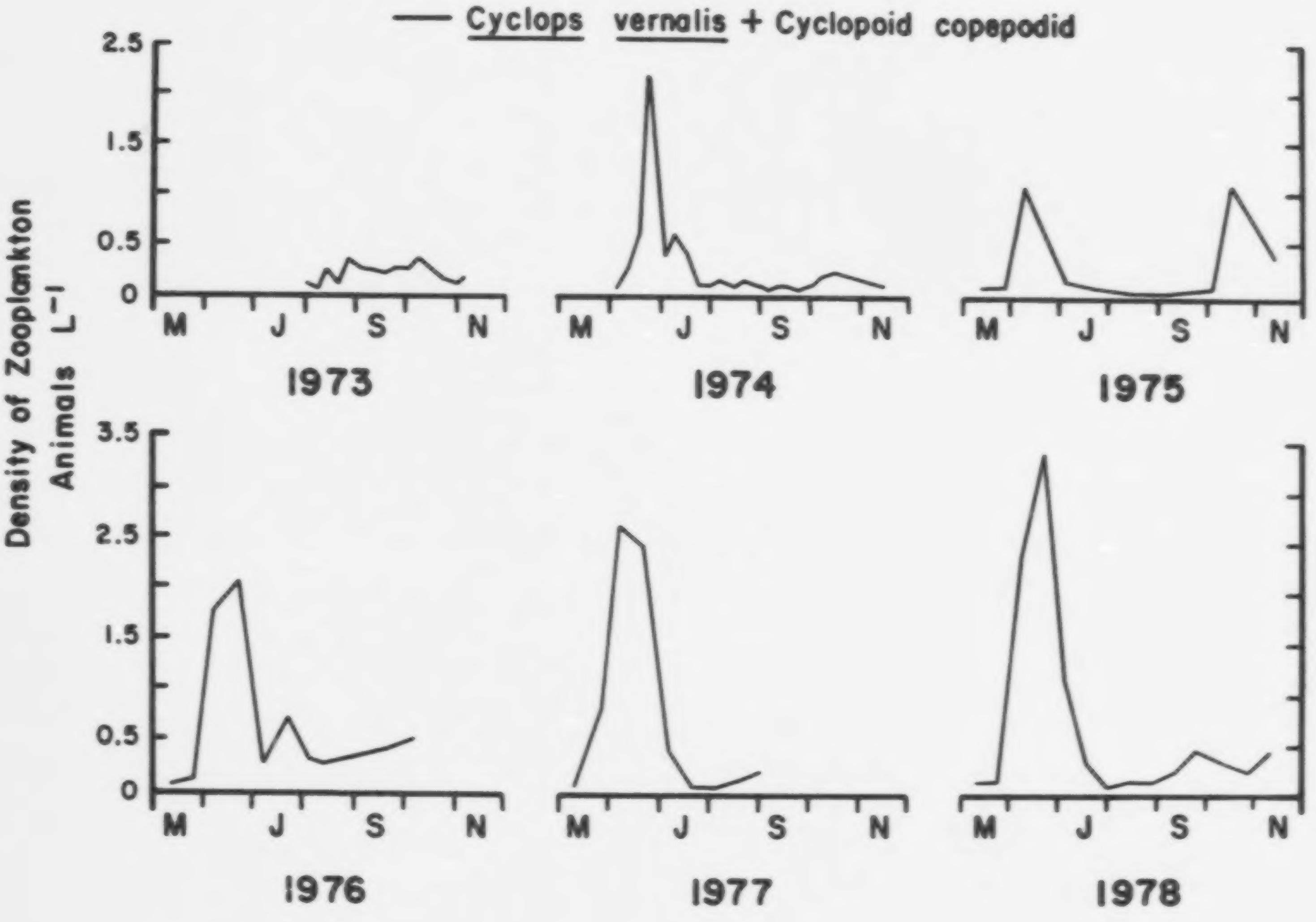


Fig. 1-10

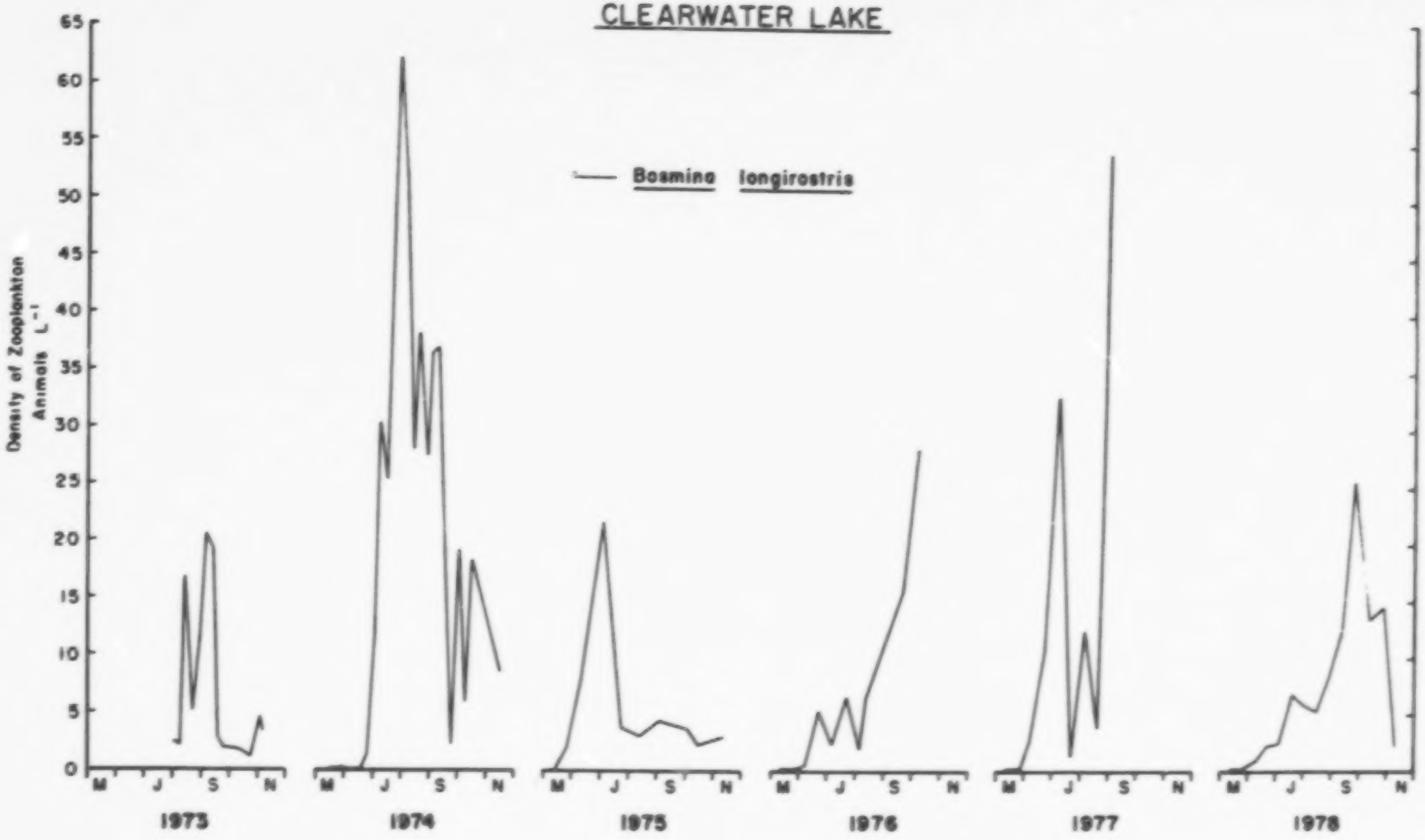

CLEARWATER LAKE
Bosmina longirostris
Density of Zooplankton
Animals L⁻¹
65
60
55
50
45
40
35
30
25
20
15
10
5
0
M
J
S
N
1973
1974
1975
1976
1977
1978

Fig.1-11

CHAPTER 2

ATMOSPHERIC DEPOSITION OF MAJOR IONS, NUTRIENTS, AND TRACE METALS IN THE SUDBURY AREA

D.S. Jeffries

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A. Introduction

Material may enter a lake via terrestrial drainage, precipitation (wet or dry), gaseous deposition, regeneration from the lake sediments (reviewed by Gorham 1961) and/or an anthropogenic point source. The importance of the atmospheric component of the total input is dependent on several factors including lake area relative to drainage basin area, bedrock and surficial deposit geochemistry, vegetation type and land use, etc. In particular, the relative insolubility of the bedrock (Appendix 2) and consequent minimal interaction with precipitation, results in a greater potential importance for the precipitation input in the Sudbury area. Various workers have determined the ion and nutrient budgets for lakes located on the Canadian Shield and discussed the importance of the precipitation input (Scheider et al. 1979b). In general, the precipitation input is especially important to the hydraulic, total P, N, and H^+ budgets. None of these lakes were in the Sudbury area, however. Little consideration has been given to the heavy metal deposition into Shield lakes. Scheider et al. (1981) have shown that bulk deposition of Cu, and Ni (and SO_4^{2-}) is elevated in the immediate Sudbury area relative to a background location (Muskoka-Haliburton) due to the influence of local mining/smelting operations. Jeffries and Snyder (1981) have shown that deposition of Zn and Fe is also elevated. These findings plus the possibility of elevated entrainment of surface dust from the basins of lakes near Sudbury (due to the sparcity of vegetation; Appendix 2) suggest that atmospheric inputs directly to the lakes' surfaces may be very important.

Wet deposition is collected only during a precipitation event (i.e. excluding all between-event dry fallout) and provides information on the chemistry of rain and snow. However, in order to measure inputs to an ecosystem from the atmosphere, collection of bulk deposition is more appropriate (Galloway and Likens 1978). Bulk deposition is operationally defined as that which falls in a continuously open collector (Whitehead and Feth 1964) and thus contains both wet precipitation and an unknown fraction of the particulate, aerosol and gaseous material which eventually reaches the earth's surface. Despite the uncertainty of the dry input component and the greater potential for sample contamination (Galloway and Likens 1976, 1978), bulk deposition probably best approximates the atmospheric loading to lake basins.

The purpose of this chapter is to provide best estimates of atmospheric deposition of major ions, nutrients, and heavy metals into the drainage basins and surfaces of the SES lakes. The estimates will be derived through consideration of the data obtained from our bulk and wet-only precipitation sampling network along with information from the Air Resources Branch. Sources of variability in the deposition (spatial and temporal) will be discussed as well as the relative importance of wet and dry depositional components.

B. Study Area and Precipitation Collection Methodology

The general geological setting of the area is described in Appendix 2. The unique feature of the Sudbury terrain is the large, elliptical, layered intrusion which contains the copper-nickel sulphide deposits which have been mined and locally smelted for several decades. Smelting practices employed in the early portions of this century denuded the local terrain of forest cover for up to at least a 5 km radius from the smelters (Hutchinson and Whitby 1977). Precipitation collectors were located on, or adjacent to most study lakes. Sampler locations are shown in Appendix 2 while details of collector design, sampling schedules, methodologies, and parameter selection are given in Appendix 1. Also given in Appendix 1 and in Scheider et al. (1981) is the statistical rationale for grouping collectors into 3 stations (North, Center, and South). Subsequent discussion of atmospheric deposition is in terms of these stations.

C. Results and Discussion

i. Composition of Bulk Deposition and Wet-only Precipitation - General Observations

A summary of the composition of bulk deposition and wet-only precipitation samples is given in Table 2-1. In Table 2-1 and throughout this chapter, ion concentrations or deposition have been expressed on an equivalent basis (eg. meq L^{-1} or meq m^{-2}) to facilitate relative comparisons. Nutrient and heavy metal parameters are expressed on a mass basis (mg L^{-1} or mg m^{-2}) except NO_3^- and NH_4^+ which are also given in meq when considering relative ion abundance and charge balance. Note that the concentration of elements in precipitation is best estimated from wet-only data since the bulk samples contain an unknown fraction of the between-event dry fallout. The relative importance of the dry fraction is reflected in the difference between bulk and wet-only values and is discussed in Section C (vi) below.

Concentrations ranged from 1 to 4 orders of magnitude for both bulk and wet samples, depending on parameter. In particular, the range for bulk and wet H^+, and bulk total P, Fe, Cu, Ni, and Zn was ~3 orders of magnitude while the remaining parameters generally exhibited a two order of magnitude variation or less. The ranges for Cu, Ni, and Fe were increased by large reduction in deposition of these metals experienced during the shutdown of

Table 2-1. Range, number of samples (n), and mean concentration of ions, nutrients, and heavy metals in bulk deposition and wet-only precipitation* samples collected at Sudbury North, Center and South for 1976-1979 Ion concentrations are in meq L^{-1} and nutrient and heavy metal concentrations are in mg L^{-1}.

		Sudbury North			Sudbury Center			Sudbury South	
Parameter	Range	n	Mean	Range	n	Mean	Range	n	Mean
bulk H^+	0.001-0.251	105	0.051	0.002-0.316	167	0.058	0.002-0.316	146	0.062
wet H^+	0.002-0.200	43	0.055	0.025-0.251	34	0.071			
bulk Ca^{++}	0.002-0.099	87	0.026	0.002-0.250	150	0.038	0.002-0.078	133	0.029
wet Ca^{++}	0.001-0.050	43	0.022	0.004-0.067	32	0.028			
bulk Mg^{++}	0.001-0.041	87	0.007	0.001-0.045	146	0.009	0.001-0.082	131	0.007
wet Mg^{++}	0.008-0.0164	43	0.005	0.008-0.016	33	0.007			
bulk Na^+	0.006-0.083	84	0.023	0.001-0.174	142	0.040	0.005-0.252	121	0.012
wet Na^+	0.004-0.039	43	0.012	0.000-0.047	33	0.014			
bulk K^+	0.000-0.034	85	0.003	0.000-0.020	146	0.003	0.000-0.037	125	0.004
wet K^+	0.003-0.004	41	0.002	0.001-0.008	35	0.002			
bulk $SO_4^=$	0.002-0.250	103	0.080	0.016-0.354	166	0.076	0.015-0.210	139	0.091
wet $SO_4^=$	0.010-0.177	42	0.067	0.019-0.207	33	0.083			
bulk Cl^-	0.001-0.045	88	0.008	0.001-0.068	147	0.026	0.001-0.087	126	0.011
wet Cl^-	0.001-0.020	42	0.005	0.002-0.019	34	0.008			
bulk total P	0.001-0.445	100	0.0397	0.001-0.414	165	0.041	0.001-0.650	137	0.476
wet total P	0.001-0.050	42	0.0127	0.003-0.052	32	0.018			
bulk NO_3^--N	0.042-3.150	84	0.552	0.065-1.70	129	0.594	0.065-2.52	102	0.615
wet NO_3^--N	0.077-2.475	30	0.440	0.11 -1.20	26	0.507			
bulk NH_4^--N	0.010-1.20	100	0.375	0.072-1.71	158	0.490	0.035-2.42	132	0.473
wet NH_4^--N	0.024-0.90	41	0.330	0.132-1.38	33	0.467			
bulk TKN	0.021-4.50	100	0.656	0.125-2.65	145	0.748	0.132-4.40	129	0.778
wet TKN	0.080-1.64	39	0.525	0.26 -1.35	30	0.596			
bulk Fe	0.010-0.480	95	0.068	0.01 -2.60	157	0.267	0.010-1.90	138	0.173
wet Fe	0.010-0.190	41	0.040	0.01 -0.31	34	0.061			
bulk Mn	0.001-0.110	46	0.010	0.001-0.060	95	0.010	0.002-0.034	95	0.008
wet Mn	0.001-0.028	29	0.005	0.002-0.015	29	0.006			
bulk Al	0.004-0.680	97	0.044	0.008-2.20	158	0.107	0.002-0.440	142	0.059
wet Al	0.004-0.180	43	0.024	0.004-0.18	36	0.038			
bulk Cu	0.001-0.240	102	0.030	0.001-1.600	176	0.182	0.001-0.830	149	0.089
wet Cu	0.001-0.054	42	0.013	0.001-0.170	36	0.050			
bulk Ni	0.001-0.093	98	0.007	0.002-0.780	175	0.073	0.001-0.720	147	0.045
wet Ni	0.001-0.023	42	0.005	0.002-0.091	36	0.023			
bulk Zn	0.001-0.530	102	0.059	0.001-0.410	174	0.056	0.001-0.370	144	0.051
wet Zn	0.002-0.064	43	0.008	0.002-0.160	36	0.017			
bulk Pb	0.003-0.120	45	0.021	0.004-0.190	86	0.031	0.004-0.150	80	0.029
wet Pb	0.004-0.056	30	0.017	0.008-0.074	27	0.024			

*wet-only precipitation samples collected between May and November of 1977, 78 and 79.

smelting operations of Inco Ltd. between Sept. 1978 - May 1979.

On an equivalent basis, the major ions in bulk deposition were in the order $H^+ > Ca^{2+} = Na^+ = NH_4^+ > Mg^{2+} > K^+$ for the cations and $SO_4^{2-} > NO_3^- > Cl^-$ for the anions. The relative importance of the cations at Sudbury is different from that found elsewhere. Our results indicating that H^+ is the most important cation and Mg^{2+} and K^+ are the least important is in agreement with Scheider _et al_. (1979b) for Muskoka-Haliburton and Likens _et al_. (1977) for New Hampshire. However, the order of the intermediate cations (Ca^{2+}, Na^+, NH_4^+) is different in each case, probably due to local factors. Schindler _et al_. (1976) and Kramer (1976) reported that Ca^{2+} and Mg^{2+} were the dominant cations in their precipitation samples although this disparity with our results may reflect the different sampling location and methodologies. The order of anion dominance is the same as that reported by others for areas underlain by the Canadian Shield (Scheider _et al_., 1979b; Schindler _et al_., 1976; Kramer, 1976; Swanson, 1976; Beamish and Van Loon, 1977; Likens _et al_., 1977)

ii. _Bulk and Wet-only Deposition_

Tables 2-2 to 2-4 give the monthly bulk deposition values of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- (meq m^{-2}) for Sudbury North, Centre, and South respectively for the period January 1976 to June, 1980. Tables 2-5 to 2-7 give the corresponding information for total P, NO_3^--N, NH_4^+-N, TKN (mg m^{-2}) and Tables 2-8 to 2-10 for Fe, Mn, Al, Cu, Ni, Zn, Pb (mg m^{-2}). Precipitation depth is included with each table. The monthly wet-only deposition of ions, nutrients, and metals for Sudbury North and Center is similarly given in Tables 2-11 to 2-16.

In order to obtain a complete bulk deposition record from

Table 2-2: Monthly bulk deposition* of ions (meq m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05	2.62					6.09		62.[illegible]
76/06	2.98					5.61		52.[illegible]
76/07	6.06					9.39		87.0
76/08	5.04					9.06		111.[illegible]
76/09	6.24					4.50		142.[illegible]
76/10								
76/11								
76/12								
77/01	3.41	1.92	0.278			2.01		48.2
77/02	6.67	1.18	0.409		0.190	4.34	0.734	71.[illegible]
77/03								
77/04								
77/05	6.80	3.32	1.338					[illegible]
77/06	4.74	2.51	0.981	2.51	0.476	10.38	0.730	49.[illegible]
77/07	8.69	2.70	1.180	2.38	0.258	6.28	0.644	35.[illegible]
77/08	5.81	2.66	1.751	2.11	0.173	4.76	0.875	81.6
77/09	12.76	3.72	0.993	2.35	0.293	7.99	0.851	146.[illegible]
77/10	4.68	1.68	0.292	1.93	0.212	5.60	0.571	64.[illegible]
77/11	4.89	1.96	0.641	2.70	0.293	5.87	0.924	78.[illegible]
77/12	5.32	0.84	0.173	2.02	0.151	2.19	1.070	34
78/01	4.14	1.07	0.221	1.64	0.161	2.32	0.890	61.[illegible]
78/02	2.44	1.23	0.252	1.07	0.157	2.24	0.606	30.[illegible]
78/03	3.10	1.73	0.584	3.59	0.269	5.75	0.821	52.[illegible]
78/04	3.33	1.99	0.820	5.50	0.340	8.31	0.938	66.[illegible]
78/05	2.29	2.14	0.703	4.34	0.923	8.38	0.743	55.[illegible]
78/06	1.96	1.58	0.404	1.73	0.726	5.89	0.520	41.[illegible]
78/07	3.59	2.90	0.597	3.29	0.500	6.27	0.334	69.[illegible]
78/08	4.86	3.24	0.480	3.42	0.298	7.11	0.718	113.[illegible]
78/09	7.49	2.42	0.485	2.27	0.179	8.92	0.540	128.[illegible]
78/10	5.07	2.35	0.521	1.12	0.120	6.69	0.448	80.6
78/11	1.14	1.72	0.218	1.58	0.072	2.10	0.298	67.1
78/12	2.25	0.83	0.148	1.31	0.093	2.75	0.362	68.[illegible]
79/01	1.47	0.09	0.024	0.99	0.072	1.42	0.425	56.[illegible]
79/02	3.71	0.49	0.067	1.36	0.005	2.58	0.362	40.[illegible]
79/03	6.68	1.48	0.228	*1.78*	0.135	5.84	0.641	78.[illegible]
79/04	14.32	2.40	0.330	2.25	0.255	11.03	0.665	155.7
79/05	4.54	2.05	0.538	0.42	0.240	7.01	0.420	76.4
79/06	7.18	2.67	0.860	0.58	0.345	10.21	0.650	72.9
79/07	7.20	1.36	0.267	0.73	0.100	6.55	0.584	160.[illegible]
79/08	6.53	1.03	0.241	0.15	0.122	7.05	0.439	67.2
79/09	4.84	1.18	0.344	0.22	0.107	6.12	0.581	52.[illegible]
79/10	9.71	1.80	0.307	0.68	0.129	10.50	0.618	105.[illegible]
79/11	6.54	0.96	0.220	0.94	0.233	7.93	1.474	75.4
79/12	3.18	0.73	0.050	0.16	0.015	0.69	0.922	60.[illegible]

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-3: Monthly bulk deposition* of ions (meq m^{-2}) and precipitation depth (mm) at Sudbury Center from January 1976 to December 1979.

PERIOD	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	DEPTH
76/01								
76/02	[illegible]	2.18				4.54		72.7
76/03		4.04						81.0
76/04								75.7
76/05	2.75					8.38		82.3
76/06	1.45					7.98		46.5
76/07	2.97					15.20		57.6
76/08	3.45					11.99		64.9
76/09	13.61					17.51		151.9
76/10	0.95					6.38		49.1
76/11								
76/12	2.12	2.92	0.312		0.140	6.57	1.216	48.6
77/01	4.14	2.26	0.529		0.225	6.69	1.726	54.2
77/02	5.13	2.24	0.438		0.178	7.08	1.446	57.0
77/03								
77/04								
77/05	2.53	3.26	0.908	2.42	0.718	11.19	1.257	38.3
77/06	3.79	2.20	0.735	2.57	0.334	7.23	0.857	52.6
77/07	7.97	7.63	1.011	3.62	0.244	9.00	1.102	107.9
77/08	11.75	5.37	1.518	3.27	0.277	9.50	1.304	117.1
77/09	16.11	6.05	0.929	5.06	0.263	11.34	1.321	131.1
77/10	5.34	6.29	0.552	2.78	0.190	5.90	0.868	77.8
77/11	5.71	2.26	0.495	3.62	0.109	5.16	0.793	71.6
77/12	5.38	1.54	0.197	3.06	0.175	6.07	1.347	80.6
78/01	5.98	1.27	0.385	2.12	0.156	7.73	1.548	64.9
78/02	3.97	1.60	0.585	3.42	0.125	7.07	1.474	42.5
78/03	3.62	2.17	0.744	3.67	0.139	7.53	1.632	33.1
78/04	3.79	1.23	0.392	7.47	0.224	*6.44*	1.079	50.7
78/05	4.18	2.84	0.511	6.63	0.728	10.92	1.105	85.2
78/06	3.56	5.10	1.294	3.24	0.666	11.25	0.999	54.4
78/07	4.19	2.99	0.628	2.43	0.290	7.46	0.442	58.6
78/08	6.80	3.40	0.556	2.18	0.300	10.23	0.520	117.2
78/09	6.27	2.51	0.444	2.25	0.257	7.29	0.731	105.1
78/10	4.15	2.51	0.728	0.94	0.105	4.14	0.519	55.8
78/11	1.98	1.78	0.344	1.51	0.077	2.82	0.882	59.1
78/12	2.28	1.54	0.288	3.19	0.090	3.17	1.864	82.1
79/01	1.87	3.20	0.077	3.20	0.038	2.56	1.622	57.8
79/02	2.96	0.80	0.036	1.61	0.011	2.57	0.956	35.6
79/03	6.40	1.43	1.250	1.84	0.097	5.42	1.215	81.0
79/04	11.44	2.79	0.404	3.62	0.205	10.15	0.831	157.5
79/05	*(7.51)*	*(2.62)*	*(0.584)*	*(2.06)*	*(0.246)*	*(8.71)*	*(1.00)*	38.7
79/06	7.58	2.45	0.764	0.50	0.288	7.27	0.456	40.0
79/07	3.92	1.52	0.437	0.33	0.129	5.18	0.253	41.5
79/08	6.70	1.59	0.464	0.20	0.129	7.45	0.473	71.1
79/09	3.76	2.19	0.669	0.22	0.083	6.99	0.185	45.0
79/10	5.19	1.76	0.466	0.35	0.098	7.73	0.341	67.7
79/11	5.04	1.08	0.219	0.63	0.114	5.46	0.805	72.0
79/12	3.09	0.96	0.266	0.89	0.114	4.36	0.929	52.4

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-4: Monthly bulk deposition* of ions (meq m^{-2}) and precipitation depth (mm) at Sudbury South from January 1976 to December 1979.

PERIOD	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	DEPTH
76/01								
76/02	3.31	1.24				4.32		83.0
76/03								
76/04								
76/05	3.90					8.30		81.8
76/06	2.61					7.99		47.7
76/07	3.29					6.27	0.597	49.7
76/08	5.01					8.35		72.8
76/09	13.42					23.44		155.1
76/10								53.0
76/11								
76/12	2.66	2.57	0.712			4.84		46.0
77/01	4.91	1.78	0.302			3.90		48.5
77/02	5.38	2.39	0.346		0.200	5.57	2.493	67.1
77/03	5.39	3.78	0.734		0.361	8.43	7.710	95.8
77/04								
77/05								
77/06	*6.92*	3.04	0.764	3.55	1.018	*9.21*	0.590	55.7
77/07	15.48	4.27	1.181	6.14	1.075	12.81	0.947	155.4
77/08	10.55	2.49	0.927	3.49	0.542	10.35	0.866	111.3
77/09	8.83	4.10	0.416	4.77	0.281	8.09	0.430	123.6
77/10	5.93	4.37	0.372	3.79	0.236	6.85	0.593	91.5
77/11	5.06	2.58	0.477	2.30	0.273	5.17	0.524	68.3
77/12	5.62	1.85	0.229	2.45	0.348	4.89	1.272	88.5
78/01	4.83	1.14	0.251	1.18	0.159	*4.56*	0.901	65.4
78/02	2.41	0.52	0.158	0.91	0.067	1.70	0.729	22.1
78/03	2.50	0.94	0.388	0.68	0.121	2.62	0.532	31.4
78/04	1.60	1.22	0.391	9.13	0.607	7.15	1.946	48.4
78/05	2.92	2.29	1.033	10.66	1.381	9.27	1.931	94.5
78/06	1.60	2.04	0.473	1.81	0.294	3.51	1.148	42.4
78/07	6.39	3.23	0.756	2.28	0.431	6.20	0.806	64.6
78/08	6.64	3.19	0.570	3.40	0.375	8.48	0.625	106.7
78/09	6.67	3.41	0.589	2.63	0.422	7.34	1.201	118.4
78/10	5.73	1.71	0.759	1.31	0.502	4.95	1.006	57.5
78/11	2.20	1.14	0.240	0.79	0.108	2.08	0.422	49.6
78/12	2.05	0.80	0.239	2.20	0.080	2.41	0.971	80.0
79/01	1.80	0.38	0.048	1.62	0.008	1.72	0.304	49.6
79/02	3.11	0.42	0.070	0.83	0.005	3.16	0.512	38.4
79/03	5.26	1.46	0.253	1.18	0.060	4.94	0.513	77.6
79/04	11.41	2.54	0.362	2.60	0.214	9.64	0.525	156.7
79/05	*(7.62)*	*(2.52)*	*(0.560)*	*(1.55)*	*(0.270)*	*(8.45)*	*(1.04)*	37.1
79/06	3.83	2.49	0.759	0.49	0.326	7.26	0.433	48.2
79/07	3.80	1.08	0.310	0.25	0.136	4.65	0.266	41
79/08	2.20	1.16	0.298	0.17	0.100	2.28	0.568	30.1
79/09	4.28	1.87	0.568	0.17	0.087	6.79	0.431	52.4
79/10	6.26	1.55	0.315	0.32	0.099	6.77	0.356	78.8
79/11	4.90	1.05	0.227	0.44	0.109	5.06	0.998	79.4
79/12	2.92	0.73	0.207	0.48	0.086	3.83	0.639	46.5

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-5: Monthly bulk deposition* of nutrients (mg m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	Total P	NO_3^--N	NH_4^+-N	TKN	DEPTH
76/01					
76/02					
76/03					
76/04					
76/05	3.19	53.2	26.9	43.2	62.5
76/06	3.42	33.5	19.8	38.0	52.5
76/07	4.04	45.6	32.5	69.4	87.0
76/08	6.20	47.3	36.2	76.0	111.9
76/09	9.27	48.9	34.0	75.9	142.7
76/10					
76/11					
76/12					
77/01	0.72	39.9	14.8	15.9	48.2
77/02	1.34	62.1	26.7	30.4	71.1
77/03					
77/04					
77/05					28.5
77/06	16.67	50.4	29.1	186.0	49.2
77/07	2.93	68.8	30.3	56.0	95.6
77/08	2.95	45.8	44.5	42.8	81.6
77/09	4.10	42.4	27.5	36.4	106.3
77/10	1.11	42.7	23.2	39.9	74.2
77/11	0.96	52.0	22.1	39.9	78.9
77/12	*0.96*	42.8	19.2	*20.7*	84.3
78/01	*1.15*	39.1	17.8	*22.7*	61.6
78/02	0.09	31.3	14.4	23.3	30.7
78/03	*3.40*	42.6	*26.8*	57.3	52.6
78/04	*5.80*	47.9	*33.7*	81.8	66.5
78/05	*7.38*	42.9	31.1	82.1	55.5
78/06	4.94	25.9	26.6	62.4	41.7
78/07	5.27	35.3	30.8	70.6	99.9
78/08	2.37	34.2	24.7	48.1	119.7
78/09	1.56	49.6	37.8	52.5	128.8
78/10	0.99	53.5	29.6	37.8	80.6
78/11	0.58	27.8	19.3	24.7	67.1
78/12	0.37	44.2	20.8	33.4	68.9
79/01	0.08	22.9	5.0	11.0	58.3
79/02	0.13	14.0	9.9	16.0	40.9
79/03	0.56	36.5	27.1	39.4	78.2
79/04	0.89	74.2	57.5	72.5	155.7
79/05	4.48	38.7	43.9	64.3	76.4
79/06	3.21	47.6	48.2	39.0	72.9
79/07	1.35	24.4	23.8	31.2	160.2
79/08	1.17	38.7	31.2	41.2	67.2
79/09	0.91	27.5	29.6	28.2	52.8
79/10	1.58	74.5	57.8	71.8	105.5
79/11	0.42	53.4	*36.0*	28.4	75.4
79/12	0.50	5.5	20.6	26.6	60.6

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicisized in the table.

Table 2-6: Monthly bulk deposition* of nutrients (mg m^{-2}) and precipitation depth (mm) at Sudbury Center from January 1976 to December 1979.

PERIOD	Total P	NO_3^--N	NH_4^+-N	TKN	DEPTH
76/01					
76/02	0.51				72.7
76/03	1.70			37.3	81.0
76/04	2.79				75.7
76/05	7.01				82.3
76/06	4.47	24.8	45.8	64.3	46.5
76/07	4.19	24.7	54.6	66.1	57.6
76/08	5.59	34.9	46.9	88.3	64.9
76/09	4.71		43.9	70.7	151.9
76/10					49.1
76/11					
76/12	0.83	43.7	24.4	33.3	48.6
77/01	7.55	56.0	40.0	83.1	54.2
77/02	4.28	52.2	37.5	64.3	57.0
77/03					
77/04					
77/05	7.76	39.0	29.1		38.3
77/06	2.50	33.1	39.2	57.2	53.6
77/07	3.86	37.1	43.0	71.4	107.9
77/08	4.57	34.9	45.6	56.1	117.1
77/09	2.12	43.8	51.0	*71.8*	131.1
77/10	0.89	52.3	36.6	52.1	77.8
77/11	0.74	46.0	17.5	35.8	71.6
77/12	1.28	59.3	26.8	35.6	80.6
78/01	1.24	44.9	33.4	49.1	64.9
78/02	0.91	45.6	43.6	60.8	43.5
78/03	0.80	60.8	61.8	83.2	33.1
78/04	0.97	44.8	31.0	56.3	50.7
78/05	*10.51*	64.2	28.6	*73.5*	85.2
78/06	16.35	59.1	39.1	81.6	54.4
78/07	5.41	36.6	27.4	56.4	58.6
78/08	3.58	47.3	35.6	54.0	117.2
78/09	2.00	42.9	37.5	67.3	105.1
78/10	1.01	52.7	29.3	30.7	55.8
78/11	0.71	40.5	22.2	31.7	59.1
78/12	0.84	57.8	36.1	54.8	82.1
79/01	0.26	32.1	14.2	26.3	57.8
79/02	0.21	26.7	10.9	20.3	35.6
79/03	0.81	58.9	32.4	48.4	81.0
79/04	1.26	72.4	43.7	64.3	157.5
79/05	*(2.76)*	*(45.3)*	*(35.1)*	*(52.0)*	38.7
79/06	4.26	41.0	29.7	39.7	40.0
79/07	3.85	25.9	20.8	26.9	41.5
79/08	1.68	38.7	33.5	48.7	71.1
79/09	1.14	38.1	43.1	41.1	45.0
79/10	1.41	52.3	39.4	46.8	67.7
79/11	0.55	64.9	32.3	40.5	72.0
79/12	0.38	45.8	26.5	31.6	52.4

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-7: Monthly bulk deposition* of nutrients (mg m^{-2}) and precipitation depth (mm) at Sudbury South from January 1976 to December 1979.

PERIOD	Total P	NO_3^--N	NH_4^+-N	TKN	DEPTH
76/01					
76/02	0.91				83.0
76/03					
76/04					
76/05	10.74				81.8
76/06	7.73	26.1	54.9	83.4	47.7
76/07	3.47	18.7	24.8	45.8	49.7
76/08	3.70		48.2	62.2	72.8
76/09	14.11		84.1	208.2	155.1
76/10		21.1			53.0
76/11					
76/12	0.50	43.9	25.4	32.6	46.8
77/01	0.56	43.5	19.3	25.9	48.5
77/02	2.68	55.0	29.5	35.9	67.1
77/03	1.67	71.1	44.1		95.8
77/04					
77/05					
77/06	*6.51*	42.4	*40.2*	*101.6*	55.7
77/07	5.84	54.6	56.0	121.1	155.4
77/08	5.17	39.4	40.2	63.2	111.3
77/09	4.28	49.4	36.4	*52.7*	123.6
77/10	1.87	58.3	36.9	*53.4*	91.5
77/11	1.10	46.4	23.9	36.7	68.3
77/12	1.34	71.7	31.4	51.8	88.5
78/01	0.69	34.9	37.4	37.6	65.4
78/02	0.26	27.1	13.7	23.7	22.1
78/03	0.35	21.1	21.4	26.7	31.4
78/04	2.04	42.7	21.7	45.3	48.4
78/05	9.33	85.8	*51.0*	117.7	94.5
78/06	9.75	21.9	9.2	30.4	42.4
78/07	6.84	38.3	*30.6*	48.6	64.6
78/08	5.82	34.3	26.5	52.2	106.7
78/09	5.57	42.8	50.9	99.1	118.4
78/10	6.87	59.5	42.6	80.8	57.5
78/11	0.52	35.4	16.9	33.1	49.6
78/12	0.34	50.7	18.2	33.3	80.0
79/01	0.12	24.1	7.1	15.6	49.6
79/02	0.24	27.2	11.8	21.4	38.4
79/03	0.58	51.2	29.2	40.8	77.6
79/04	2.11	68.7	45.1	65.5	156.7
79/05	*(3.36)*	*(43.2)*	*(31.6)*	*(55.0)*	37.1
79/06	4.62	39.2	31.6	44.5	48.2
79/07	2.60	20.0	18.4	*26.8*	41.3
79/08	1.65	35.2	25.8	30.5	80.1
79/09	1.57	41.5	40.6	35.6	52.9
79/10	1.22	51.6	32.2	32.8	78.8
79/11	0.69	63.0	30.1	40.3	79.4
79/12	0.54	40.6	22.0	25.9	46.5

*for the period 77/06-79/12, missing values were estimated (see text) and are italicized in the table.

Table 2-8: Monthly bulk deposition* of heavy metals (mg m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	FE	MN	AL	CU	NI	ZN	PB	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05	4.89			4.35	1.05	4.37		62.5
76/06	4.32			5.21	0.90	4.98		52.5
76/07	6.28		2.14	5.66	0.90	5.71		87.0
76/08	6.01		3.39	4.02	1.35	6.02		111.9
76/09	4.63		15.95	3.07	0.45	8.63		142.7
76/10								
76/11								
76/12								
77/01	2.27	0.145	1.25	2.36	0.77	0.92		48.2
77/02	6.86	0.346	2.71	1.03	0.17	2.88		71.1
77/03								
77/04								
77/05								28.5
77/06	3.42	0.610	2.74	2.65	0.29	6.88	*(1.68)*	49.2
77/07	3.50	0.818	1.98	8.89	0.20	7.72	0.70	95.6
77/08	4.60	0.576	3.62	5.51	0.53	11.94	*2.01*	81.6
77/09	4.49	0.374	1.46	6.76	0.65	8.05	*2.31*	106.3
77/10	7.04	0.977	3.15	7.39	0.66	4.21	*1.92*	74.2
77/11	17.23	2.183	9.03	6.51	0.70	7.38	*3.18*	78.9
77/12	21.50	0.843	15.60	0.93	0.17	0.76	*(1.68)*	84.3
78/01	21.50	0.631	10.09	1.31	0.55	1.64	*(1.68)*	61.6
78/02	*6.28*	0.338	3.07	1.60	0.92	2.46	*0.75*	30.7
78/03	5.50	*0.694*	3.57	1.52	0.80	1.89	1.51	52.6
78/04	5.32	*0.732*	3.59	1.26	0.60	1.13	1.46	66.5
78/05	4.53	*0.735*	4.93	1.07	0.38	7.23	1.51	55.5
78/06	2.62	*0.624*	2.73	0.52	0.20	9.02	2.37	41.7
78/07	3.48	*0.785*	2.06	0.84	0.46	6.73	2.16	99.9
78/08	1.60	*0.598*	2.26	0.44	0.37	1.92	2.15	119.7
78/09	2.57	*0.471*	0.84	0.48	0.24	1.60	2.15	128.8
78/10	2.51	0.343	1.44	0.24	0.18	1.36	0.95	80.6
78/11	4.39	0.687	5.08	0.07	0.23	0.68	1.14	67.1
78/12	9.15	*0.330*	4.36	0.13	0.15	0.57	0.84	68.9
79/01	6.73	0.123	0.66	0.12	0.09	0.26	0.30	58.3
79/02	5.08	0.077	1.04	0.04	0.06	0.38	0.60	40.9
79/03	6.83	*0.513*	3.98	0.53	0.12	0.97	*(1.68)*	78.2
79/04	10.68	0.483	8.68	0.15	0.45	1.99	0.24	155.7
79/05	5.64	0.733	5.85	0.13	0.11	0.84	3.23	76.4
79/06	3.15	0.710	3.30	0.61	0.58	0.74	2.73	72.9
79/07	2.50	0.284	2.22	0.28	0.16	0.71	2.15	160.2
79/08	2.42	0.226	1.03	0.58	0.21	0.80	2.61	67.2
79/09	3.89	0.396	0.71	0.22	0.08	0.76	0.51	52.8
79/10	7.73	0.818	3.47	1.39	1.01	7.15	2.95	105.5
79/11	13.64	2.159	2.27	8.18	10.57	21.59	3.41	75.4
79/12	17.56	0.545	2.54	1.76	1.82	8.48	1.21	60.6

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-9: Monthly bulk deposition* of heavy metals (mg m^{-2}) and precipitation depth (mm) at Sudbury Center from January 1976 to December 1979.

PERIOD	FE	MN	AL	CU	NI	ZN	PB	DEPTH
76/01								
76/02	87.20		33.43	71.21	21.80	1.45		72.7
76/03	24.30		6.72	129.62	49.42	6.32	9.72	81.0
76/04				79.12	31.04	9.45		75.7
76/05				20.58	10.96	11.52		82.3
76/06	12.66			11.22	3.33	6.01		46.5
76/07	24.97		4.63	19.28	7.46	3.68		57.6
76/08	26.90		10.12	15.10	6.03	2.96		64.9
76/09	31.69		10.02	33.16	15.60	5.56		151.9
76/10	44.31	1 623		12.68	5.19	2.30		49.1
76/11								
76/12	19.39	0.450	7.45	93.42	26.79	1.92		48.6
77/01	28 98	0.464	6.02	62.75	18.68	2.17		54.2
77/02	25.97	0.525	6.59	51.03	15.07	1.88		57.0
77/03								
77/04								
77/05								38.3
77/06	8.74	0.482	5.10	10.74	4.48	3.30	3.83	53.6
77/07	8.89	0.622	5.04	8.32	2.59	2.62	3.63	107.9
77/08	9.64	0.551	5.30	14.56	3.26	5.30	*2.57*	117.1
77/09	8.08	0.571	2.57	16.34	5.51	10.47	*3.06*	131.1
77/10	10.49	0.460	2.37	7.77	5.62	5.58	*2.18*	77.8
77/11	10.89	0.588	3.66	14.55	6.43	2.84	*2.41*	71.6
77/12	50.20	0.772	9.25	35.13	16.03	1.93	*3.63*	80.6
78/01	112.68	0.884	7.28	69.42	25.76	2.22	*5.79*	64.9
78/02	89.22	0.684	3.97	56.50	18.96	1.63	*4.93*	43.5
78/03	59.68	0.506	2.53	43.07	14.24	1.33	*4.07*	33.1
78/04	*18.05*	*0.528*	1.56	13.08	4.63	0.86	2.46	50.7
78/05	15.03	1.021	4.61	7.70	2.75	10.64	*2.53*	85.2
78/06	9.26	*0.901*	3.99	8.72	3 38	8.01	*2.41*	54.4
78/07	3.43	*0.547*	3.10	5.00	1.92	2.94	1.35	58.6
78/08	3.70	*0.562*	3.49	2.30	1.15	1.70	1.36	117.2
78/09	4.95	*0.511*	1.74	1.87	0.96	1.64	1.24	105.1
78/10	3.80	0.347	2.78	0.34	0.22	1.49	0.86	55.8
78/11	9.58	0.472	8.23	0.43	0.26	0.85	1.23	59.1
78/12	9.16	*0.429*	5.58	0.55	0.16	0.65	1.27	82.1
79/01	12.64	0.262	3.51	0.48	0.28	1.76	1.33	57.8
79/02	5.43	0.134	1.93	0.27	0.11	0.64	1.46	35.6
79/03	11.68	*0.489*	9.44	0.43	0.24	1.05	*1.39*	81.0
79/04	13.85	0.395	8.76	0.65	0.20	1.41	*1.43*	157.5
79/05	*19.40*	*(0.634)*	*(7.21)*	*(4.10)*	*(2.43)*	*(1.11)*	*(2.27)*	38.7
79/06	24.95	1.004	22.21	7.55	4.67	0.80	2.23	40.0
79/07	24.13	0.664	31.27	10.40	5.18	0.67	1.60	41.5
79/08	16.32	0.353	5.27	12.24	3.57	0.95	1.94	71.1
79/09	19.09	0.677	3.10	6.87	2.99	2.07	0.97	45.0
79/10	31.88	0.724	4.81	11.62	5.65	8.43	2.55	67.7
79/11	30.45	1.025	4.89	7.76	5.44	7.78	2.55	72.0
79/12	28.42	0.842	11.48	8.40	3.07	6.60	1.55	52.4

*for the period 77/06-79/12, missing values have been estimated (see text) and are italicized in the table.

Table 2-10: Monthly bulk deposition* of heavy metals (mg m^{-2}) and precipitation depth (mm) at Sudbury South from January 1976 to December 1979.

PERIOD	FE	MN	AL	CU	NI	ZN	PB	DEPTH
76/01								
76/02	17.43	0.830	2.08	28.23	12.45	1.66		83.0
76/03								
76/04								
76/05				21.28	6.30	8.63		81.8
76/06	9.37			15.55	2.84	6.34		47.7
76/07	7.28	0.265	2.83	10.62	2.06	5.63		49.7
76/08	7.19		2.59	11.11	3.20	7.75		72.8
76/09	17.24		4.41	29.99	8.31	14.46		155.1
76/10	11.13	0.382	1.99	6.32	2.54	5.98		53.0
76/11								
76/12	32.00	0.259	3.81	31.00	11.76	0.97		46.8
77/01	37.42	0.272	4.36	32.03	13.13	1.62		48.5
77/02	27.51	0.562	9.95	21.31	9.47			67.1
77/03	37.44	0.949	19.33	16.07	6.59	2.23		95.8
77/04								
77/05								
77/06	*(8.93)*	*(0.494)*	*3.53*	*(6.11)*	*(1.30)*	*9.48*	*(1.80)*	55.7
77/07	8.93	0.748	6.60	6.11	1.30	8.32	5.20	155.4
77/08	4.28	0.384	2.53	4.13	1.23	7.77	*2.82*	111.3
77/09	3.80	0.352	0.69	4.73	1.35	4.85	*2.34*	123.6
77/10	8.80	0.468	4.53	5.63	2.11	5.06	*3.17*	91.5
77/11	12.08	0.504	4.55	6.59	2.48	5.39	*3.34*	68.3
77/12	43.43	0.716	5.02	12.94	47.76	1.16	*5.33*	88.5
78/01	88.38	0.439	3.71	16.05	14.36	1.16	*5.80*	65.4
78/02	14.97	0.172	2.14	10.49	4.14	0.87	*3.54*	22.1
78/03	7.54	0.126	3.02	7.54	2.48	0.75	*2.93*	31.4
78/04	5.87	*0.335*	1.33	3.78	1.53	1.97	1.40	48.4
78/05	7.69	*1.344*	2.91	3.34	1.52	19.96	*1.77*	94.5
78/06	5.36	*0.275*	3.15	2.05	0.86	3.34	*1.30*	42.4
78/07	5.29	*0.495*	3.26	2.57	1.27	6.02	*2.05*	64.6
78/08	1.79	*0.372*	3.08	0.71	0.26	3.58	*1.51*	106.7
78/09	16.12	*0.358*	2.04	0.59	0.28	2.11	0.39	118.4
78/10	6.19	*0.567*	2.92	0.37	0.23	3.94	0.79	57.5
78/11	4.33	0.349	1.99	0.23	0.11	1.68	0.84	49.6
78/12	5.23	*0.422*	4.76	0.40	0.14	0.57	0.87	80.0
79/01	2.88	*0.129*	0.80	0.30	0.17	0.40	0.56	49.6
79/02	3.12	0.136	2.02	0.24	0.10	0.73	0.82	38.4
79/03	4.83	*0.467*	5.81	0.10	0.25	1.06	*1.83*	77.6
79/04	7.61	0.404	6.67	0.46	0.22	1.37	*2.88*	156.7
79/05	*(6.23)*	*(0.494)*	*(3.98)*	*(1.08)*	*(0.55)*	*(1.08)*	*(1.80)*	37.1
79/06	4.86	0.692	5.05	1.71	0.87	0.79	3.83	48.2
79/07	3.06	0.249	2.83	2.31	1.34	0.37	2.24	41.3
79/08	7.09	0.274	2.04	2.66	1.01	0.80	2.45	80.1
79/09	7.88	0.458	4.94	2.22	0.82	0.98	0.70	52.9
79/10	16.31	0.596	4.31	3.43	2.26	2.89	2.24	78.8
79/11	17.91	1.471	3.80	4.92	6.62	16.62	2.79	79.4
79/12	18.09	0.787	3.47	5.22	2.82	18.63	1.83	46.5

*for the period 77/06-79/12, missing values were estimated (see text) and are italicized in the table.

Table 2-11: Monthly wet-only deposition of ions (meq m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05								
76/06								
76/07								
76/08								
76/09								
76/10								
76/11								
76/12								
77/01								
77/02								
77/03								
77/04								
77/05	1.94	0.73	0.301	0.42	0.062		0.275	24.4
77/06	3.14	1.72	0.467	1.73	0.095	5.12	0.221	56.2
77/07	10.94	1.27	0.502	0.67	0.136	5.81	0.270	95.6
77/08	5.44	2.13	0.977	1.43	0.201	4.23	0.839	86.4
77/09	14.24	4.22	0.693	2.45	0.162	6.95	0.384	126.4
77/10	4.27	1.30	0.252	0.83	0.097	3.17	0.388	61.3
77/11	2.70	1.62	0.265	0.83	0.207	3.25	0.451	64.4
77/12								
78/01								
78/02								
78/03								
78/04								
78/05	1.25	0.99	0.245	0.60	0.051	3.10	0.112	19.8
78/06	2.57	1.60	0.362	1.06	0.109	6.65	0.250	52.1
78/07	3.91	2.05	0.356	1.38	0.138	5.70	0.299	105.2
78/08	3.99	0.71	0.150	0.56	0.113	4.89	0.202	110.9
78/09	7.31	2.95	0.415	1.46	0.145	5.46	0.606	119.3
78/10	5.95	1.63	0.381	0.74	0.141	4.83	0.529	82.0
78/11								
78/12								
79/01								
79/02								
79/03								
79/04								
79/05	1.99	0.94	0.188	0.29	0.080	2.53	0.203	47.7
79/06	6.52	2.03	0.526	0.38	0.093	9.24	0.466	77.8
79/07	7.54	1.14	0.246	0.53	0.071	5.97	1.321	155.4
79/08	6.53	1.19	0.185	0.15	0.064	6.34	0.390	67.2
79/09	4.84	0.59	0.163	0.09	0.041	5.44	0.202	52.8
79/10	3.58	0.14	0.065	0.03	0.015	3.16	0.120	64.9
79/11								
79/12								

Table 2-12: Monthly wet-only deposition of ions (meq m^{-2}) and precipitation depth (mm) at Sudbury Center from January 1976 to December 1979.

PERIOD	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05								
76/06								
76/07								
76/08								
76/09								
76/10								
76/11								
76/12								
77/01								
77/02								
77/03								
77/04								
77/05	1.93	0.56	0.154	0.46	0.048	1.10	0.591	18.8
77/06	6.45	1.53	0.596	1.30	0.131	4.92	0.529	51.3
77/07	10.36	3.10	0.909	1.96	0.200	6.90	0.716	102.0
77/08	13.44		1.298	1.25	0.464	5.58	0.665	106.6
77/09	12.07	1.87	0.514	1.16	0.160	5.79	0.565	125.1
77/10	4.30	2.06	0.314	0.48	0.098	4.13	0.280	76.3
77/11	1.54	0.44	0.090		0.028	1.82	0.123	21.8
77/12								
78/01								
78/02								
78/03								
78/04								45.3
78/05	0.59							9.3
78/06	2.96	3.14	1.266	0.71	0.394	6.07	0.435	68.9
78/07	3.51	2.69	0.415	1.59	0.152	5.60	0.308	60.5
78/08	5.88	3.21	0.353	3.04	0.170	9.55	0.472	115.8
78/09	4.80	2.35	0.453	1.30	0.184	5.73	0.520	106.6
78/10	4.86	1.32	0.239	0.50	0.075	3.50	0.275	58.3
78/11	0.64	0.40	0.100	0.07	0.013	0.81	0.083	10.1
78/12								
79/01								
79/02								
79/03								
79/04								
79/05	1.19	0.77	0.157	0.40	0.079	2.26	0.275	23.8
79/06	3.76	1.87	0.453	0.66	0.129	6.37	0.631	38.7
79/07	3.36	0.94	0.204	0.60	0.066	3.91	0.388	36.8
79/08	6.05	1.31	0.304	0.17	0.101	6.59	0.657	76.5
79/09	4.46	1.17	0.378	0.13	0.025	6.03	0.184	48.6
79/10	5.30	1.27	0.323	0.23	0.063	6.12	0.323	71.6
79/11								
79/12								

Table 2-13: Monthly wet-only deposition of nutrients (mg m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	Total P	NO_3^--N	NH_4^+-N	TKN	DEPTH
76/01					
76/02					
76/03					
76/04					
76/05					
76/06					
76/07					
76/08					
76/09					
76/10					
76/11					
76/12					
77/01					
77/02					
77/03					
77/04					
77/05	0.33	12.2	12.9	19.5	24.4
77/06	1.48	8.2	23.5	53.9	56.2
77/07	2.91	50.0	27.3	33.7	95.6
77/08	0.92	41.9		14.2	86.4
77/09	2.37	36.6	26.8	7.3	126.4
77/10	0.33	29.4	20.2	28.1	61.3
77/11	0.13	30.5	26.9	27.7	64.4
77/12					
78/01					
78/02					
78/03					
78/04					
78/05	0.47	17.7	17.5	24.0	19.8
78/06	1.24	29.0	28.3	42.6	52.1
78/07	1.70	29.5	25.6	44.8	105.2
78/08	0.58	25.8	20.8	50.5	110.9
78/09	0.73	39.4	32.3	39.5	119.3
78/10	0.52	53.4	29.1	37.0	82.0
78/11					
78/12					
79/01					
79/02					
79/03					
79/04					
79/05	0.81	12.9	11.2	61.7	47.7
79/06	0.64	42.2	42.9	35.3	77.8
79/07	0.83	25.1	23.6	26.3	155.4
79/08	0.52	38.1	26.3	44.6	67.2
79/09	0.41	24.8	27.9	31.8	52.8
79/10	0.25	19.9	14.3	14.6	64.9
79/11					
79/12					

Table 2-14: Monthly wet-only deposition of nutrients (mg m^{-2}) and precipitation depth (mm) at Sudbury Centre from January 1976 to December 1979.

PERIOD	Total P	NO_3^--N	NH_4^+-N	TKN	DEPTH
76/01					
76/02					
76/03					
76/04					
76/05					
76/06					
76/07					
76/08					
76/09					
76/10					
76/11					
76/12					
77/01					
77/02					
77/03					
77/04					
77/05	0.39	9.2	6.0	14.9	18.8
77/06	0.39	31.8	23.6	30.3	51.3
77/07	2.80	53.4	45.1	66.0	102.0
77/08	4.20	37.5	35.2	48.1	106.6
77/09	0.69	30.0	44.1		125.1
77/10	0.33	24.1	26.9	16.9	76.3
77/11		15.8	9.8	12.4	21.8
77/12					
78/01					
78/02					
78/03					
78/04					45.3
78/05	0.42	8.7	10.8	12.5	9.3
78/06	2.02	39.8	19.0	58.9	68.9
78/07	0.90	33.5	17.4	25.1	60.5
78/08	0.79	54.8	31.7	33.6	115.8
78/09	0.82	36.8	34.7	47.8	106.6
78/10	0.32	44.8	23.3	32.6	58.3
78/11	0.12	12.2	7.9	7.5	10.1
78/12					
79/01					
79/02					
79/03					
79/04					
79/05	1.12	14.1	13.9	18.3	23.8
79/06	1.94	38.0	32.2	36.3	38.7
79/07	1.11	21.2	17.9	21.0	36.8
79/08	0.75	36.1	45.9	38.9	76.5
79/09	0.70	34.8	35.8	34.7	48.6
79/10	1.12	49.9	34.7	40.6	71.6
79/11					
79/12					

Table 2-15: Monthly wet-only deposition of heavy metals (mg m^{-2}) and precipitation depth (mm) at Sudbury North from January 1976 to December 1979.

PERIOD	FE	MN	AL	CU	NI	ZN	PB	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05								
76/06								
76/07								
76/08								
76/09								
76/10								
76/11								
76/12								
77/01								
77/02								
77/03								
77/04								
77/05	0.98	0.122	0.37	1.15	0.39	0.49		24.4
77/06	3.21	0.263	2.12	1.56	0.35	1.91	0.12	56.2
77/07	1.44	0.403	1.12	1.60	0.38	0.92	0.58	95.6
77/08	1.48	0.774	0.92	1.44	0.36	0.40		86.4
77/09	1.74	0.494	1.26	2.86	0.62	0.70		126.4
77/10	1.92	0.258	1.01	1.39	0.29	0.39		61.3
77/11	2.51	0.288	1.51	1.34	0.38	0.63		64.4
77/12								
78/01								
78/02								
78/03								
78/04								
78/05	3.57		3.57			0.32	1.11	19.8
78/06	5.97		4.82	1.15	0.49	0.52	1.80	52.1
78/07	4.18		2.24	1.38	0.62	0.62	1.36	105.2
78/08	0.91		2.05	0.43	0.46	0.39	1.08	110.9
78/09	2.15	1.216	0.93	0.83	0.45	0.93	1.11	119.3
78/10	3.74		1.41	0.40	0.29	0.64	0.87	82.0
78/11								
78/12								
79/01								
79/02								
79/03								
79/04								
79/05	1.43	0.204	1.18	0.08	0.05	0.17	1.84	47.7
79/06	2.20	0.417	2.42	0.31	0.35	0.30	1.85	77.8
79/07	3.68	0.816	2.35	0.36	0.31	0.92	1.98	155.4
79/08	2.66	0.183	2.24	0.46	0.23	0.47	1.70	67.2
79/09	1.75	0.198	0.70	0.17	0.15	0.26	0.45	52.8
79/10	1.54	0.120	0.21	0.34	0.96	0.20	1.20	64.9
79/11								
79/12								

Table 2-16: Monthly wet-only deposition of heavy metals (mg m^{-2}) and precipitation depth (mm) at Sudbury Center from January 1976 to December 1979.

PERIOD	FE	MN	AL	CU	NI	ZN	PB	DEPTH
76/01								
76/02								
76/03								
76/04								
76/05								
76/06								
76/07								
76/08								
76/09								
76/10								
76/11								
76/12								
77/01								
77/02								
77/03								
77/04								
77/05	1.32	0.106	0.93	1.07	0.53	0.26		18.8
77/06	1.32	0.378	1.42	1.56	0.94	0.43	0.71	51.3
77/07	1.91	0.701	2.59	4.25	1.28	0.67	1.28	102.0
77/08	3.62	0.426	2.57	12.46	3.21	1.30		106.6
77/09	4.55	0.500	1.25	11.60	5.26	0.92		125.1
77/10	5.49	0.176	1.24	5.19	3.24	8.77		76.3
77/11	1.11	0.065	0.68	1.03	1.31	0.22		21.8
77/12								
78/01								
78/02								
78/03								
78/04			1.04	7.25	3.17	0.59	2.27	45.3
78/05			0.71	0.22	0.13	0.22	0.26	9.3
78/06	5.33		2.33	5.02	2.07	1.23	0.47	68.9
78/07	1.42		1.91	4.55	1.72	0.69	1.45	60.5
78/08	1.82		2.37	1.11	1.01	0.98	1.62	115.8
78/09	1.86		2.48	1.30	0.64	0.94	1.40	106.6
78/10	2.53	0.116	1.68	0.31	0.20	0.61	0.93	58.3
78/11	0.41	0.111	0.81	0.07	0.06	0.13	0.26	10.1
78/12								
79/01								
79/02								
79/03								
79/04								
79/05	1.19	0.214	1.98	0.10	0.10	0.64	1.76	23.8
79/06	8.19	0.493	4.35	0.88	0.49	0.64	2.53	38.7
79/07	8.23	0.212	3.28	1.48	0.74	0.21	1.06	36.8
79/08	6.48	0.205	2.36	2.66	1.04	0.46	1.73	76.5
79/09	3.22	0.264	0.40	0.28	0.08	0.08	0.21	48.6
79/10	5.38	0.367	2.61	4.02	2.00	2.29	1.54	71.6
79/11								
79/12								

June 1977 to December 1979, missing values for a given parameter were estimated from the multiple linear regression of its three highest correlates which had the measured values necessary to allow the calculation (ie. no value was estimated from a previously estimated datum) and which gave a significant regression ($p<0.05$). Most regressions were in fact significant at the $p=0.001$ level. For example, the deposition of Na^+ for March, 1979 at Sudbury North (Table 2-2) was estimated from the multiple linear regression of Na^+ against K^+, NO_3^-, and Ca^{2+} ($r^2 = 0.58$, $p=0.001$, $n=30$). Values estimated by regression are italicized in Tables 2-2 to 2-10.

When the multiple linear regression approach could not be used (eg. no correlating parameters or no significant regression), the data were either estimated by simply using the overall average monthly deposition for those parameters which do not exhibit seasonal trends (Cl^-, NO_3^-, NH_4^+, Al, Mn, and Pb; discussion in following section) or the average of the months before and after for parameters that do exhibit seasonal trends. Since no May, 1977 value was available for estimating the June deposition of Fe, Cu and Ni at Sudbury South, the value for July 1977 was used. The deposition values estimated by these means are italicized and in brackets in Tables 2-2 to 2-10.

An overall indicator of the data quality for ions is given by the degree of balance of cations and anions. We were unable to measure a balance in the deposition of anions and cations at Sudbury. The charge balance in monthly deposition $\{[\Sigma\text{cations} - \Sigma\text{anions}/(\Sigma\text{cations} + \Sigma\text{anions})/2] \times 100\}$ ranged from 0.3% to 95% (bulk) and 2 to 82% (wet) with the cations being in excess in almost all cases. The balance for annual bulk deposition was 17%, 10%, and

24% for 1978, and 15%, 7%, and 6% for 1979, for Sudbury North, Center, and South respectively. The cations and anions are more closely balanced on an annual basis than those reported by Scheider et al. (1979b) for Muskoka-Haliburton (30-40% for 1976-78) where similar methods were used and a cation excess also observed. The imprecision of the analytical methods for these very low concentration samples is the most likely explanation for the imbalance. In 1979, the analytical methods were specifically adapted for precipitation samples, which resulted in the improved charge balance observed for this year.

Large variation in monthly bulk deposition observed at Sudbury (Table 2-17) is due to both natural causes (as manifested in year to year and seasonal variation) and anthropogenic factors (primarily operation and/or shutdown of smelters).

iii. Seasonal Variation

Seasonal patterns of deposition are apparent for several parameters. Precipitation depth is generally greatest during summer and autumn and least during the winter months. This pattern is of particular importance since deposition of several ionic species has been found to vary with the amount of precipitation (Pearson and Fisher, 1971; Likens et al., 1977). Hence the summer maxima visually apparent for the deposition of H^+, Ca^{2+}, Mg^{2+}, Na^+(?), K^+, SO_4^{2-}, total-P and TKN probably reflect the precipitation pattern. In addition, the reduced contribution from local wind-blown surface materials during periods of snow cover may also be a factor for all of the above parameters except H^+ and SO_4^{2-}. Hydrogen ion and SO_4^{2-} are primarily deposited after atmospheric transport from distance sources (Scheider et al., 1981). Scheider et al. (1979b) found a similar seasonal pattern for

Table 2-17: Variation in monthly bulk deposition at Sudbury North, Center and South (1976-1980).

Parameter		Sudbury North					Sudbury Center					Sudbury South				
		Mean(n)	Min.	Max.	Std. Dev.	Median	Mean(n)	Min.	Max.	Std. Dev.	Median	Mean(n)	Min.	Max.	Std. Dev.	Median
Depth(mm)		78.3(39)	28.5	160	31.7	72.9	70.2(44)	33.1	157	29.6	62.0	72.9(42)	22.1	158	33.3	66.3
H^+	meq m^{-2}	5.29(39)	1.14	14.3	2.86	4.86	4.94(41)	0.95	16.1	3.23	3.93	5.22(39)	1.60	15.5	3.21	4.90
Ca^{2+}		1.82(34)	0.09	3.73	0.86	1.77	2.71(36)	0.80	7.63	1.63	2.26	2.02(35)	0.38	4.37	1.13	1.85
Mg^{2+}		0.500(34)	0.024	1.75	0.390	0.396	0.576(34)	0.04	1.52	0.335	0.503	0.463(34)	0.048	1.18	0.276	0.380
Na^+		1.88(30)	0.15	5.50	1.30	1.69	2.48(31)	0.20	7.47	1.73	2.42	2.40(30)	0.17	10.7	2.52	1.71
K^+		0.239(32)	0.005	0.923	0.194	0.184	0.221(34)	0.011	0.738	0.175	0.177	0.316(32)	0.005	1.38	0.321	0.225
SO_4^{2-}		5.97(38)	0.69	11.0	2.76	6.11	7.56(40)	2.56	17.5	3.21	7.25	6.50(38)	1.70	23.4	3.81	6.23
Cl^-		0.685(32)	0.298	1.47	0.242	0.647	1.00(34)	0.18	1.86	0.445	0.977	1.04(33)	0.27	7.71	1.29	0.639
total P	mg m^{-2}	2.68(33)	0.08	16.7	3.27	1.35	2.85(41)	0.21	16.3	3.02	1.68	3.33(39)	0.12	14.1	3.44	1.87
NO_3^--N		42.3(38)	5.45	74.5	14.5	42.8	45.3(37)	24.7	72.4	12.0	44.8	43.2(37)	18.7	85.8	16.3	42.4
NH_4^+-N		28.4(35)	5.01	57.8	11.7	27.1	35.1(38)	10.9	61.8	10.8	35.8	31.6(35)	7.12	84.1	15.6	29.5
TKN		49.8(36)	11.0	186	30.7	40.5	52.1(36)	20.3	88.3	17.8	53.0	53.0(33)	15.6	208	38.2	40.3
Fe		6.65(37)	1.60	21.5	5.17	4.89	24.9(39)	3.4	113	24.7	16.3	14.0(39)	1.79	88.4	16.0	7.69
Mn		0.642(24)	0.077	2.18	0.531	0.561	0.633(27)	0.134	1.62	0.300	0.570	0.494(26)	0.126	1.47	0.299	0.422
Al		3.97(36)	0.66	15.9	3.66	2.90	7.21(38)	1.56	33.4	7.08	5.07	3.98(38)	0.69	19.3	3.12	3.21
Cu		2.31(38)	0.04	8.89	2.61	1.17	23.4(42)	0.3	130	29.6	11.4	8.38(40)	0.10	32.0	9.37	4.82
Ni		0.767(38)	0.06	10.6	1.68	0.450	8.60(42)	0.11	49.4	10.3	4.92	4.46(40)	0.10	47.8	8.06	1.80
Zn		4.25(38)	0.26	21.6	4.34	2.22	3.65(42)	0.64	11.5	3.13	2.19	4.57(39)	0.37	20.0	5.08	2.23
Pb		1.68(22)	0.24	3.41	0.97	1.51	2.27(19)	0.86	9.72	1.99	1.55	1.80(15)	0.39	5.20	1.37	1.40

all these parameters (except H^+) at Muskoka-Haliburton. Chloride does not appear to exhibit a seasonal trend although occasionally high deposition in winter probably reflects useage of de-icing salts on local roads. This will also complicate the Na^+ deposition pattern resulting in the uncertainty noted above. Nitrate-N, NH_4^+ -N, Al, and Mn do not show seasonal patterns of deposition. Other parameters exhibit seasonal patterns which reflect the combination of meteorological factors and local industrial sources. Jeffries and Snyder (1981) have shown that during periods of smelter operation, deposition of Cu and Ni is maximum during summer for Sudbury North and during winter for Sudbury Center and South. This difference arises from the change in prevailing wind direction (southerly in summer, northerly in winter) and the position of the 381 m stack 5 km north of the Sudbury Center station.

Although Zn emission is of the same order of magnitude as Cu and Ni (Ministry of the Environment 1979), summer maxima were observed at all three stations for this metal. This observation may reflect smaller average particle size for Zn compared to Cu and Ni (see Section C (v)) and thus the pattern of Zn deposition follows the precipitation pattern as it did for the ions.

No consistent pattern of Fe deposition was discernable at Sudbury North during periods of smelter operation. However, for Sudbury Center and Sudbury South winter maxima were observed. Since Fe is emitted from the 381 m stack at an even greater rate than Cu and Ni (Ministry of the Environment 1979) and is similarly concentrated in the largest size fraction, (see Section C (v)) their parallel pattern of deposition is reasonable.

An insufficient number of analyses for Pb were performed to allow recognition of any temporal pattern of deposition for the element.

iv. Spatial Variability

Analysis of Variance (ANOVA) results (discussed in Appendix 1) showed that there was significant spatial variability over the SES area for SO_4^{2-}, total P, Cu, Ni, Fe, and Al. Differences in bulk deposition between collectors for SO_4^{2-}, Cu, Ni, and Fe may be attributed to relative proximity to the smelting operations (Scheider et al., 1981; Jeffries and Snyder 1981). Reasons for the variability in total-P and Al are unclear but may be related to factors specific to the collector site. For all other parameters except those noted above, there is a statistically uniform deposition suggesting that the factors influencing their deposition are consistent over the SES study area.

Annual bulk deposition rates at Sudbury North, Center, and South for major ions, nutrients, and heavy metals are compared to those measured in other studies in Tables 2-18 to 2-20 respectively. Scheider et al. 1981 have shown that deposition of SO_4^{2-}, Cu and Ni was reduced during the period of smelter inactivity from September 1978 to April 1979. Hence for comparison purposes, only bulk deposition values from July 1977 - June 1978 were presented in Tables 2-18 to 2-20.

Although H^+ deposition at the three Sudbury stations exceeds the Muskoka-Haliburton values (Table 2-18; Scheider et al., 1979b), Scheider et al. 1981 have subsequently shown that there is no statistical difference among the four of them. The Sudbury values are at the top end of the range reported for other Shield locations. Magnesium and K^+ loadings are similar to the Muskoka-Haliburton data and within range for other locations. Calcium also follows this pattern except for Sudbury Center where the elevated deposition may reflect the greater availability of

Table 2-18. Annual bulk deposition (meq m^{-2} yr^{-1}) of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and precipitation depth (mm) at Sudbury North, Center, and South for July 1977 - June 1978. Additional data for Muskoka-Haliburton and elsewhere are presented for comparison.

Parameter	Sudbury North	Sudbury Center	Sudbury South	Muskoka-Haliburton[1]	Other Shield Areas[2]	Elsewhere[3]
H^+	60.4	77.8	67.3	54.6, 58.2	10 -55.9	-
Ca^{2+}	23.3	43.9	27.8	33.8, 28.9	18.9-70.5	3.99-109
Mg^{2+}	8.02	8.61	6.30	8.37, 6.66	5.6-72.1	4.93-40.3
Na^+	32.5	45.9	47.3	17.5, 17.1	5.5-45.6	3.04-249
K^+	3.96	3.50	5.38	4.06, 2.91	2.4-20.7	2.05-46.5
SO_4^{2-}	65.6	97.9	77.5	61.6, 64.1	20.7-55.6	8.75-131
Cl^-	9.46	14.6	11.8	8.85, 6.46	7.5-18.8	-
Precipitation Depth (mm)	830	918	943			

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[1] two annual values corresponding to Aug. '76 - July '77, and Aug. '77 - July '78 (Scheider et al. 1979b).

[2] data summarized by Scheider et al. (1979b) for other areas in Ontario underlain by Precambrian Shield.

[3] data summarized by Likens et al. (1977) for other catchments throughout the world.

Table 2-19. Annual bulk deposition (mg m^{-2} yr^{-1}) of total-P, NO_3^--N, and TKN at Sudbury North, Center and South for July 1977 - June 1978. Additional data for Muskoka-Haliburton and elsewhere are presented for comparison.

Parameter	Sudbury North	Sudbury Center	Sudbury South	Muskoka-Haliburton[1]	Other Shield Areas[2]	Elsewhere[3]
total P	-[5]	44.4	42.0	41.5, 28.9	5.6-77.2	3.6- 60
NO_3^--N	524	593	553	347, 473	281	-
NH_4^+-N	310	458	385	348, 389	-	-
TKN	552	728	670	667, 611	372	-
total N[4]	1076	1321	1223	1015, 1084	495-1600	110-2070

[1] two annual values corresponding to Aug. '76 - July '77, and Aug. '77 - July '78 (Scheider et al. 1979b).

[2] data summarized by Scheider et al. (1979b) for other areas in Ontario underlain by Precambrian Shield.

[3] data summarized by Likens et al. (1977) for other catchments throughout the world.

[4] total N = NO_3^- + TKN.

[5] greater than 2 estimated monthly values during time period.

Table 2-20. Annual bulk deposition (mg m^{-2} yr^{-1}) of Fe, Mn, Al, Cu, Ni and Zn at Sudbury North, Center, and South for July 1977 - June 1978. Additional data[1] for North America and Europe are presented for comparison. Insufficient data for Pb was available for comparison.

Parameter	Sudbury North	Sudbury Center	Sudbury South	Muskoka Haliburton[1]	North America Median[1]		Europe Median[1]	
					Urban-Industrial	Rural	Urban-Industrial	Rural
Fe	104	393	211	101	503	219	520	178
Mn	_4	8.16	_2	7.58	4.1	2.4	20	9.4
Al	62.8	52.1	40.1	65.4	-	-	-	-
Cu	43.2	295	83.4	2.12	16	3.7	32	15
Ni	6.38	109	81.1	<1.6	-	-	31	3.2
Zn	63.4	53.4	60.6	15.7	319	47.2	103	55

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[1] data from Jeffries and Snyder (1981).

[2] greater than 2 estimated monthly values during time period.

locally entrained materials from the "vegetation-free" terrain and/or use of road treatment chemicals. This latter factor may also account for the greater Na^+ deposition experienced at Sudbury. Parallel higher Cl^- deposition suggests that at least a portion of the Ca^{2+} and Na^+ loading is due to the use of $CaCl_2$ and NaCl on roads in the urban Sudbury area. Sulphate deposition at Sudbury North and Muskoka-Haliburton are similar and slightly above the top of the range reported for other Shield locations. The SO_4^{2-} loading near the smelting operation is significantly greater than other reported values (Scheider et al., 1981).

Deposition of nutrients (Table 2-19) at Sudbury is generally comparable to loadings experienced at Muskoka-Haliburton and within range of those reported elsewhere. Only NO_3^--N deposition at the three Sudbury stations consistently exceeds the Muskoka-Haliburton value perhaps reflecting the greater vehicular source present at Sudbury.

Jeffries and Snyder (1981) have previously compared heavy metal deposition at Sudbury to Muskoka-Haliburton and other North American and European locations (see Table 2-20). Briefly, Mn and Al deposition are comparable at all sites while an inverse relationship exists between Fe deposition and distance from the 381 m stack. However, the elevation of Fe loading rates at Sudbury Center is not as high as the median values for urban-industrial environments in Europe and North America. Zinc deposition is consistent among the three Sudbury stations and comparable to median rural values, but approximately 4-fold higher than that at Muskoka-Haliburton. Copper and Ni deposition at Sudbury exhibit the same distance relationship to the 381 m stack as Fe, but the values exceed almost all others reported for urban-industrial environments elsewhere. They are also at least 20- and 4-fold higher, respectively, than central Ontario "background" as represented by Muskoka-Haliburton.

v. Influence of Local Industry

From the preceding discussion, differences in the amount of deposition of materials between the Sudbury stations and central Ontario background (Muskoka-Haliburton) could be attributed to influence by local industrial emissions, the differing geomorphology of the two areas (eg. greater bedrock exposure at Sudbury, paucity of vegetation, etc.), and/or use of road treatment chemicals. The Ni smelting industry at Sudbury is a major emitter of H^+, SO_4^{2-}, and several metals (Ministry of Environment 1979) and thus may influence the regional depositional pattern of these materials.

Scheider et al. (1981) have considered the influence of the largest source (Inco, Ltd.) on the H^+ and SO_4^{2-} deposition in the area by comparing measured bulk deposition during periods of smelter operation and shutdown. They concluded that the industry had no significant influence on the bulk H^+ deposition in the area and that only the closest station (Sudbury Center) experienced significantly elevated SO_4^{2-} deposition. The bulk deposition of H^+ and SO_4^{2-} carried into the Sudbury area by long range transport mechanisms is sufficiently large to "swamp out" the influence of the smelter emissions (except for SO_4^{2-} within 5 km of the source). It should be noted that potential changes in the dry deposition of SO_2 were not addressed in the analysis of Scheider et al. (1981).

Deposition of certain metals does show a strong industrial influence. For example, bulk deposition of Cu, Ni and Fe decreases with distance from the principal smelters. As shown in Table 2-20, maximum levels occurred at Sudbury Center (the station closest to the 381 m stack) and minimum levels at Sudbury North (the most distant station). These results support the deposition contour maps presented by Kramer (1975) which showed a roughly elliptical pattern centered around Sudbury with the long axis oriented in a SW-NE direction similar to the direction of predominating ground level winds. Hutchinson and Whitby (1977) have studied Cu and Ni levels in soils along transects leading away from the main smelter and similarly report elevated concentrations (10 to 20 fold above background) to a distance of 13.4 km. Background values were observed at distances greater than 50 km. Scheider et al. (1981) also showed that bulk Cu and Ni deposition decreased up to 2 orders of magnitude at the Sudbury stations during a period of Inco, Ltd. shutdown (Sept. 1978 to April 1979) and this decrease is clearly evident in Tables 2-8 to 2-10. The reduced deposition experienced during this period approached that at Muskoka-Haliburton. Bulk Zn deposition is reasonably uniform across the three Sudbury stations despite the fact that stack emissions are of the same order as Cu and Ni (Ministry of the Environment 1979). Jeffries and Snyder (1981) suggest that this observation reflects the different particle size of Zn emissions (1 to 2 μm) compared to Cu, Ni, and Fe (4 to >9 μm). The smaller sized Zn particles are more evenly dispersed, but the resulting deposition is still elevated relative to "background" values at Muskoka-Haliburton. Enrichment factors for Zn calculated by Jeffries and Snyder (1981) also support the presumption of an anthropogenic source of this metal.

vi. Wet Deposition

Wet-only preciptation samples were collected during the warm period of the year (April/May to October/November) when reliable operation of the battery operated collectors was assured. Although wet-only deposition exhibited a similar spatial variability as the bulk deposition, the following discussion must be considered in view of the "summer" bias present in the wet-only data.

An estimate of the relative importance of the wet and dry components of the total deposition may be obtained by comparing the wet-only and bulk values during periods of simultaneous collection. Table 2-21 presents the percent of bulk deposition measured as the wet-only fraction during "pre-shutdown" collection periods. Also included are comparable data from Muskoka-Haliburton. The percent values in Table 2-21 are likely high estimates of the relative importance of wet to total deposition since a) no winter data have been included when "natural" dry deposition (of locally entrained materials) may be at a minimum due to sealing of the ground surface with snow, and b) the bulk collector is no doubt a poor device for collecting dry gaseous deposition and has an unknown collection efficiency for dry particulates.

The percent of bulk deposition measured as the wet-only fraction often varied widely between the two stations at Sudbury. However, the data presented in Table 2-21 suggest that wet deposition during a period of smelter operation consistently exceeded dry for both stations for H^+, SO_4^{2-}, NO_3^--N, NH_4^+-N and Ni. Conversely, dry deposition of Na^+, Cl^-, total P, Fe, Cu and Zn dominated at both stations. The most important deposition type was different between the stations for all the remaining parameters (Ca^{2+}, Mg^{2+}, K^+, TKN, Mn, Al, Pb) and followed no obvious pattern, thus suggesting that site specific factors may be controlling this observation.

Wet deposition is generally much less important at Sudbury

Table 2-21. Wet-only deposition as a percent of bulk deposition at Sudbury North and Sudbury Center for ions, nutrients, and heavy metals for all months of simultaneous collection between May, 1977 and June, 1978 (eg. pre-shutdown); n is the number of months of data included in the percent value. Data from Muskoka-Haliburton is provided for comparison.

Parameter	Sudbury North %	n	Sudbury Center %	n	Muskoka Haliburton[1] %
H^+	89.7	9	82.7	8	106
Ca^{2+}	70.0	9	41.9	7	82.9
Mg^{2+}	49.0	9	68.8	7	83.7
Na^+	45.8	8	35.8	7	85.9
K^+	28.4	7	53.2	8	62.7
SO_4^{2-}	74.5	8	60.8	8	83.1
Cl^-	49.7	8	49.2	8	72.4
total P	28.1	7	20.9	6	45.9
NO_3^--N	67.1	8	61.1	9	80.4
NH_4^+-N	91.6	7	66.9	8	79.2
TKN	43.0	6	69.1	4	76.9
Fe	47.5	8	37.3	7	64
Mn	45.8	6	69.8	6	–
Al	56.8	8	39.9	8	78
Cu	31.2	7	46.8	8	157
Ni	93.8	7	51.8	8	–
Zn	9.95	8	28.3	8	61
Pb	77.7	3	27.8	2	130

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[1] data for ions and nutrients at Muskoka-Haliburton (Aug. 1976-July 1978) from Scheider et al. (1979b) and for heavy metals (Oct. 1977-Sept. 1978) from Jeffries and Snyder (1981).

than at Muskoka-Haliburton. At this latter "background" location, only the dry deposition of total P exceeds the wet contribution, and in fact the wet deposition of H^+ exceeds the bulk, that is, wet-only samples have a lower volume-weighted pH than bulk samples. The apparently excessive wet deposition of Cu and Pb at Muskoka-Haliburton (Table 2-21) probably reflects the large relative error present in the analyses due to the very low concentrations determined at this location. At Sudbury, the influence of local industrial sources and/or differences in terrain yields a situation in which the dry component of total deposition is of greater importance than is the case at the background location. This conclusion further underlines the need for using bulk collectors to measure ecosystem inputs from the atmosphere.

Cawse (1974) presented data for the percent of dry to total deposition (comparable to 100 - values in Table 2-21) for his sampling network in Britain. This network covered a range of depositional environments from rural (Plynlimon and Wraymires) to urban/industrial (Styrrup and Trebanos). The importance of the dry depositional component and difference between rural and urban/industrial environments in Britain generally compare favourably to our findings for Ca^{2+}, Pb, Fe, Mn and Zn. The percent dry of total deposition for Al and Cu at Muskoka-Haliburton falls within the range reported for Cawse's rural stations, however, for urban/industrial settings, dry inputs are relatively more important at Sudbury than at Styrrup/Trebanos. In contrast, the dry Ni component is comparatively less important at Sudbury. Finally the dry deposition of Na^+ and Cl^- is almost always less important in Britain than at either location in Ontario reflecting the greater maritime influence on the deposition of these elements in Britain.

vii. Snow Coring

Snow cores were taken along transects with the basins of Middle and Nelson Lakes during the first week of March, 1977. The average volume-weighted concentration for several parameters determined in the core samples, coefficient of variation and calculated deposition are presented in Table 2-22. Also included in Table 2-22 is the bulk deposition measured for December 1976 through February 1977 at Sudbury Center (eg. the approximate period when the snowpack was accumulating).

In accord with the ANOVA results showing a generally insignificant variance between precipitation collectors (Appendix 1) within a station, the snow cores exhibited a reasonably uniform composition within each lake basin. While precipitation data normally exhibits a large natural variability (Tables 2-1 and 2-17) the coefficient of variation for the snow cores was less than 100% except for Mg^{2+}, Cl^-, total P and Al. Differences in snow composition and deposition between Middle and Nelson Lakes followed the same trends as for bulk deposition, eg. the Middle Lake cores showing relatively elevated levels for several parameters, particularly Fe, Al, Cu and Ni.

Differences between the "winter integrated" snow core concentrations (Table 2-22) and the overall mean "bulk" concentrations (Table 2-1) are generally explained by seasonal patterns of deposition (discussed in section C (iii) and/or the effect of partial melting. There were 10 days where the maximum temperature exceeded 0°C during the period December 1 to March 6, 1977. Hence, elevated bulk deposition of Fe, Cu and Ni measured at Sudbury Center during the winter is also in evidence as elevated concentrations in the snow cores.

Table 2-22. Average volume-weighted concentration of ions (meq L^{-1}), nutrients and metals (mg L^{-1}), and coefficient of variation from snow cores collected in the Nelson Lake basin (n = 10) and the Middle Lake basin (n = 15) in March 1977. Deposition (meq m^{-2} for ions, mg m^{-2} for nutrients and metals) present in the accumulated snow pack and corresponding bulk deposition at Sudbury Center are also presented for comparison.

Parameter[1]	Nelson Lake - Sudbury North			Middle Lake - Sudbury Center			
	Mean Concentration	Coef. of Variation(%)	Deposition	Mean Concentration	Coef. of Variation(%)	Deposition	Bulk Deposition[2]
H^+	0.079	20	9.17	0.084	68	12.8	11.4
Ca^{2+}	0.029	34	4.24	0.026	20	4.69	7.40
Mg^{2+}	0.0099	141	1.17	0.0072	26	1.29	0.99
$SO_4{}^{2-}$	0.041	22	4.32	0.056	23	10.2	20.4
Cl^-	0.014	107	3.26	0.048	40	17.2	4.4
total P	0.028	93	3.25	0.030	110	5.46	12.7
$NO_3{}^-$-N	0.725	9	85.6	0.625	33	113	99.7
$NH_4{}^-$-N	0.237	18	28.0	0.337	16	60.9	71.9
TKN	0.466	16	55.0	0.557	26	101	123
Fe	0.106	50	12.5	0.597	63	108	74.3
Mn	0.011	45	1.30	0.0089	5	1.62	1.44
Al	0.040	33	4.70	0.208	137	37.5	20.1
Cu	0.041	24	4.78	0.663	23	120	207
Ni	0.014	36	1.65	0.234	25	42.3	60.5
Zn	0.013	38	1.54	0.021	24	3.85	5.97

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[1] Na^+ and K^+ were not measured in the snow core samples.

[2] deposition for 3 mo. (Dec. 1976 - Feb. 1977).

Sulphate concentrations were low in the snow core samples. Dry deposition of SO_2 was expected to increase the SO_4^{2-} concentrations in the snow relative to the bulk samples, however the reverse situation was observed (snow concentrations ~50 of bulk). We cannot account for this observation unless partial melting has preferentially removed SO_4^{2-} from the snow profile; the counter ion(s) which must also have been removed is not obvious although Na^+ and K^+ were not analyzed and deposition of the former was probably elevated during the winter months (cf Cl^-). Hydrogen ion concentrations in snow and bulk samples were similar.

The concentration and depostion of Cl^- obtained from the snow cores at Middle Lake (Table 2-22) was approximately 4-fold higher than that measured from the bulk collector. This disparity arose because the Middle Lake snow cores were taken along a transect on the terrestrial portion of the watershed which was much closer to a roadway than the "on-lake" bulk deposition collector. Contamination by de-icing salt resulted in the elevated Cl^- concentrations. Snow cores collected at Nelson Lake which were not affected by roadways were much closer to the bulk values.

viii. "Additional" Dry Deposition

Neither the wet-only nor the bulk collectors adequately sample total deposition of gaseous species such as SO_2. The magnitude of the unmeasured SO_2 deposition was estimated using measured air concentrations (M.O.E. Northeastern Region) and an average deposition velocity of 0.8 cm sec^{-1}. The range of deposition velocities in the literature is wide. Garland (1978) summarized ten studies which together showed a range of deposition velocities of 0.1-2.2 cm sec^{-1}. The use of different methods to

estimate deposition velocities partly accounted for the range in values. However, deposition velocities are thought to vary with many factors including the type of surface (water, soil, grass, forest etc.,), the pH of the surface water film, the relative humidity and the height of the vegetation canopy (Garland 1978). Garland (1978) recommended a value of 0.8 cm sec^{-1} for much of Europe but cautioned that the figure was correct only to a factor of two.

Chan et al. (1982) calculated a long-term average deposition velocity of 0.3 cm sec^{-1} to be applicable to the greater Sudbury area. Their calculations were based on the method of Sheih et al. (1979) which attempts to account for several factors affecting the deposition velocity such as land-use, biological status of the vegetation and the atmospheric stability. This method yields a value of 0.6-0.7 cm sec^{-1} for the deposition velocity over water in the Sudbury area, similar to the 0.8 cm sec^{-1} value of Garland (1978).

Based on these studies and realizing the uncertainty involved in the choice of a deposition velocity, a value of 0.8 cm sec^{-1} was applied to the study basins. This value, higher than the estimate of the regional Sudbury value (0.3 cm sec^{-1} Chan et al. 1982), was adopted because of the relatively high ratio of lake/land area and the denuded topography of some of the study basins, and is considered to be appropriate for lake surfaces primarily. The average annual SO_2 concentration (ppm) for 1977 to 1979, calculated SO_2 dry deposition (as meq SO_4^{2-} m^{-2} yr^{-1}) and the ratio of dry to bulk SO_4^{2-} deposition is given in Table 2-23.

Table 2-23. Dry deposition of SO_2 calculated from measured air concentrations[1] and a deposition velocity of 0.8 cm sec^{-1}. Air density was assumed to be 1.2 g L^{-1} for all calculations. Dry deposition is expressed as meq(SO_4^{2-})m^{-2} yr^{-1}.

Station	Period	Average SO_2 Concentration (ppm)	Dry Deposition meq(SO_4^{2-})m^{-2} yr^{-1}	Bulk Deposition meq(SO_4^{2-})$m^{-2}$$yr^{-1}$	Ratio (Dry:Bulk)
Sudbury North[2]	1977	0.006,0.011	80	-	-
	1978	0.003,0.006	46	66	0.70
	1979	0.003,0.005	39	77	0.51
Sudbury Center[3]	1977	0.008,0.015	110	-	-
	1978	0.006,0.012	85	86	0.99
	1979	0.006,0.012	85	74	1.15
Sudbury South[4]	1977	0.006	57	-	-
	1978	0.005	44	61	0.72
	1979	0.004	38	70	0.54

[1] SO_2 air concentrations provided by Northeastern Region, Ontario Ministry of the Environment.

[2] SO_2 concentrations for Rayside and Hanmer respectively; average used for subsequent deposition calculation.

[3] SO_2 concentrations for Lockerby and Ash Street respectively; average used for subsequent deposition calculation.

[4] SO_2 concentration for Burwash.

These data suggest that total sulphur inputs to the watersheds is underestimated by the bulk deposition measurement. The calculated dry deposition of SO_2 is less than the measured bulk deposition (approximately 50-70%) at the Sudbury North and South stations while at Sudbury Center, dry and bulk deposition are approximately equal. These findings are in general accord with the conclusions of Garland (1978) who estimated (for northwestern Europe) that dry deposition of SO_2 was of equal or greater significance compared to wet deposition. Our average bulk concentration of SO_4^{2-} is ~25% higher than the corresponding wet-only value. As reflected in the variability in average SO_2 concentrations, dry SO_2 deposition is more variable on an annual basis over the study area than bulk SO_4^{2-} deposition. This is reasonable in view of the fact that SO_2 concentrations are primarily influenced by local sources while SO_4^{2-} deposition is influenced to a greater extent by long range transport.

Sulphur dioxide deposition decreased during the shutdown period of Inco, Ltd. Average monthly dry deposition calculated for months of smelter operation (1978, 1979) was 4.2, 7.9, and 4.1 meq (SO_4^{2-}) m^{-2} at Sudbury North, Center, and South respectively, and declined during the months of shutdown to 2.6, 5.9 and 2.5 meq m^{-2}. Sudbury Center still exhibited the highest SO_2 deposition during the shutdown period. The lower annual dry deposition estimates for 1978, 1979 compared to 1977 (Table 2-23) occurred because the shutdown period spanned September 1978 to May 1979.

ix. Components of Strong Acidity in Precipitation

The most important strong acids contributing to the low pH of precipitation at Sudbury are sulfuric and nitric acids as indicated by the predominance of SO_4^{2-} and NO_3^-. Comparison of the mean concentrations (in equivalents) of these components (Table 2-24) in bulk deposition samples at the 3 Sudbury stations suggest that, on average, sulphuric acid contributes approximately 2-fold more to the total strong acidity than does nitric acid (SO_4^{2-}/NO_3^- ranges from 1.8 to 2.1). The nitric acid component is most important at Sudbury Center - the station closest to urban Sudbury where automotive exhaust is probably the primary source. The relative importance of the two acids is similar to that measured in Muskoka-Haliburton. Sulphuric acid may be slightly more important at Hubbard Brook, although Likens et al. (1977) present evidence that over the period of their data set (1963-1974), the nitric acid contribution to the total strong acidity increased by 2-fold. The period of sample collection at Sudbury is too short to allow a similar assessment of long term trends in NO_3^- (or SO_4^{2-}) deposition. Furthermore, the bulk deposition samples do not provide the total SO_4^{2-} input (see Chapters 5, 6) so that ratios of total SO_4^{2-} to NO_3^- must be even higher.

Comparable results were obtained for wet-only deposition, although the ion ratio was slightly greater at both Sudbury North and Sudbury Center which probably reflects the "summer-only" collection periods for the wet-only samples. They do compare favourably with the wet-only ratio at Muskoka-Haliburton however, which was calculated from year-round data. The small difference in importance of SO_4^{2-} in wet-only samples compared to bulk samples supports the conclusion that our bulk collectors do not effectively catch dry SO_4^{2-} deposition.

Seasonal variation in the bulk SO_4^{2-}/NO_3^- ratio is illustrated in Figure 2-1. The ratios vary in a similar fashion for all three stations from winter lows of ~1 to summer highs of ~3.

Table 2-24: Mean concentrations (μeq L^{-1}) of SO_4^{2-} and NO_3^- and their ratio for bulk and wet-only deposition samples collected at Sudbury North, Sudbury Center, and Sudbury South from 1976 to 1979. Similar data from Muskoka-Haliburton and Hubbard Brook are included for comparison.

Location	Sampling Period	Deposition Type	Mean Concentration (μeq L^{-1}) SO_4^{2-}	NO_3^-	Ratio (SO_4^{2-}/NO_3^-)
Sudbury North	1976–1979	Bulk	80	39	2.1
		Wet-only[1]	67	31	2.2
Sudbury Center	1976–1979	Bulk	76	42	1.8
		Wet-only[1]	83	36	2.3
Sudbury South	1976–1979	Bulk	91	44	2.1
Muskoka-Haliburton[2]	Aug, 1976– July, 1978	Bulk	83	39	2.1
		Wet-only	69	31	2.2
Hubbard Brook[3]	1963–1974	Bulk	60	24	2.5

[1] wet-only data at Sudbury North and Sudbury Center are for summer months only (1977, 1978, 1979).

[2] adapted from Scheider et al. (1979b); volume weighted mean

[3] Likens et al. (1977); volume weighted mean

The winter lows are also in general agreement with the ratio found in snow cores (0.8 for Nelson Lake and 1.2 for Middle Lake, December, 1976 to February, 1977). The seasonal variation observed for SO_4^{2-} (summer maxima, see 2C (iii) above) and lack of seasonal trends for NO_3^- deposition account for the patterns in Fig. 2-1. Hence during winter, sulphuric and nitric acids contribute almost equally to the strong acidity of bulk deposition at Sudbury, while in summer when warmer temperatures and more intense sunlight increase the oxidation rate of SO_2, sulphuric acid dominates by a factor of approximately three. The contribution of sulphuric acid to the total acid deposition is even greater.

D. Summary

1. Bulk deposition of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, TP, NO_3^-, NH_4^+, TKN, Fe, Mn, Al, Cu, Ni, Zn and Pb was measured for the period June 1977 to December 1979 for 3 stations in the Sudbury area; namely, Sudbury North (30-50 km north of Copper Cliff), Sudbury Center (4-5 km south), and Sudbury South (10-12 km south). Wet-only deposition was also measured at Sudbury North and Sudbury Center for May/June to October/November from 1977 to 1979.
2. The major cations in bulk deposition (on an equivalent basis) were $H^+ > Ca^{2+} \approx Na^+ \approx NH_4^+ > Mg^{2+} > K^+$. The major anions were in the order $SO_4^{2-} > NO_3^- > Cl^-$. The ions balanced within 17, 10 and 24% for 1978, and 15, 7 and 6% for 1979 for Sudbury North, Sudbury Center and Sudbury South, respectively. Cations were always in excess.
3. Deposition of materials in precipitation varied in time and in space. Deposition of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, TP, TKN and Zn was greatest during the summer when precipitation depth was greatest. Most of the annual Cu and Ni deposition occurred in the summer at Sudbury North, while Cu, Ni and Zn deposition was greatest in the winter at Sudbury Centre and South. Spatial variation in the deposition of SO_4^{2-}, Cu, Ni, and Fe was related to smelter emissions. Deposition rates for these substances decreased with increasing distance from the smelters.
4. Deposition rates of Al, Mn, nutrients and major ions, excepting SO_4^{2-}, were similar or only slightly higher at the Sudbury stations than rates in south-central Ontario. However,

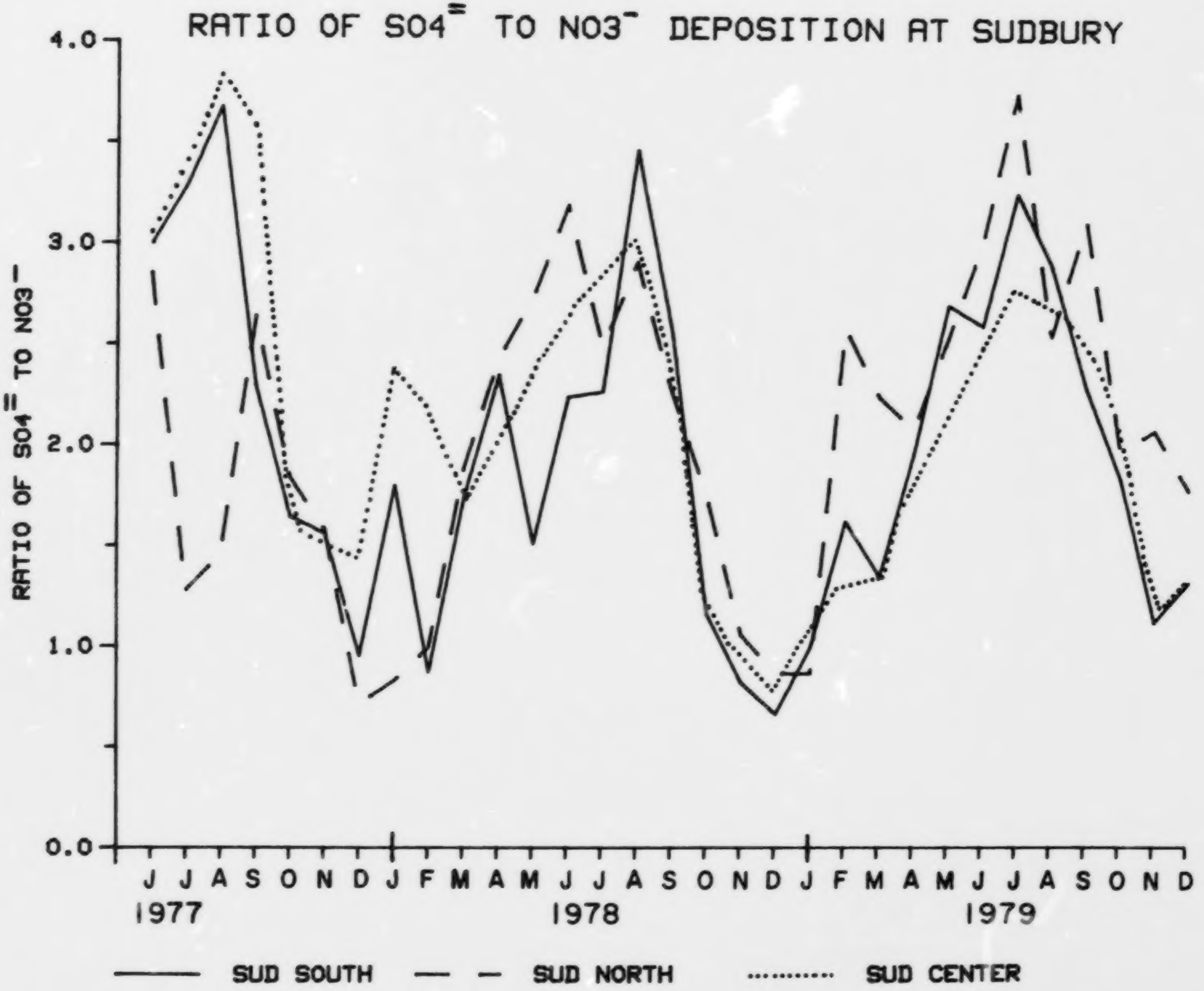
deposition rates of Cu, Ni, Zn, Fe and SO_4^{2-} were strongly influenced by local smelting activities, in fact, Cu and Ni deposition rates exceeded virtually all previously reported values for industrialized areas. Even at Sudbury North, the station with the lowest trace metal deposition rates, levels were 4-, 4- and 20-fold higher than in south-central Ontario for Zn, Ni and Cu, respectively. During a period of time when smelters of Inco Ltd. were not operating, bulk deposition rates of these metals decreased to levels typical of south-central Ontario.

5. Wet deposition exceeded dry deposition for H^+, SO_4^{2-}, NO_3^--N, NH_4^+-N and Ni at Sudbury North and Center, while dry input exceeded wet for Na^+, Cl^-, TP, Fe, Cu and Zn. The dry component of the precipitation was generally more important than in south-central Ontario.
6. Deposition rates of gaseous SO_2 were estimated as the product of atmospheric SO_2 concentrations and a deposition velocity of 0.8 cm sec^{-1}. Gaseous inputs calculated as SO_4 were 50-70% of bulk deposition at Sudbury North and South and approximately equal at Sudbury Center. The SO_2 deposition rates decreased during the shutdown at Inco Ltd.
7. Sulphuric acid contributed approximately twice as much as nitric acid to the strong acidity of bulk deposition at Sudbury, and was even more important when gaseous SO_2 inputs were considered. Seasonal variations in rates of SO_4^{2-} deposition did occur, resulting in relatively greater nitric acid contributions to total acidity in the winter. Even in the winter, however, nitric acid contributed <50% of the total strong acid inputs.

LIST OF FIGURES

Fig. 2-1. Ratio of monthly SO_4^{2-} to NO_3^- bulk deposition (both as meq m^{-2}) at Sudbury North, Center, and South, from June 1977 to December 1978. Seasonal variation in the ratio was similar at all stations, being high in summer and low in winter.

Fig.2-1



RATIO OF $SO_4^=$ TO NO_3^- DEPOSITION AT SUDBURY

CHAPTER 3

SEDIMENT CHEMISTRY AND RATES OF SEDIMENTATION IN LAKES NEAR SUDBURY, ONTARIO

P.J. Dillon and P.J. Smith

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A. Introduction

The chemical composition of lakewater reflects the inputs and outputs of materials to and from a lake and the processes occurring witnin the lake over a time scale of usually only a few years, or at most, a few decades (ie. over 2 or 3 times the length of the lake's water replacement time). Lake sediments, however, may record the processes that have occurred in the lake's watershed, airshed, and in the lake itself over the lake's entire life span. By determining the age of each layer of sediment below the sediment water interface, the corresponding sediment chemistry can be used to pinpoint in time, events that have affected the lake. In fact, by using a combination of techniques to establish the dates when specific sediments were deposited, a complete sedimentation chronology can be established.

The recent development of relatively simple dating techniques for determining the age of sediments deposited in the last few hundreds of years compliments well-established techniques applicable to rocks and sediments deposited hundreds or thousands of years before the present. The new techniques developed for dating recent sediments permit a detailed look at the effects of modern civilization on aquatic ecosystems. Studies of the sediments of specific lakes have clearly shown the impacts of early settlement and land-clearing, of agricultural practices, of industry, of transportation, etc.

Lake sediments are studied for other reasons as well. They constitute the habitat of the benthic organisms which are an integral part of the aquatic ecosystem. Sediments are often important components of the whole-lake mass balances of materials, acting as a source and/or sink for many elements and compounds.

It is well-established that the smelter operations in Sudbury have affected the chemistry of precipitation, lakes, streams and soils in the study area (see Chapters 1, 2, 5). The deposition of strong acids, some major ions and particularly metals is elevated above that considered to be the historic or background levels. In fact, the deposition of certain metals in this area is much greater than recorded elsewhere in North America (Jeffries and Snyder 1981). The metal concentrations of the study lakes are also elevated, suggesting that effects on lake sediments are likely. Unusually high levels of some metals in surficial sediments of lakes near Sudbury have been previously reported (see B, below).

Investigations of the sediments of these lakes were carried out in an attempt to determine:

1) the current accumulation rates of materials in the lakes' sediments.
2) the relationship between the elevation of copper, nickel or other trace metals in the lakes' sediments and the introduction of smelter operations in the Sudbury area.
3) other changes in the sediment that reflect changes in lake chemistry/biology, and the timing of these changes.
4) the effects of the whole-lake manipulation experiments (neutralization, fertilization) on the lakes' sediments.

B. Background

Very few studies of the sediments of lakes in the Sudbury area have been reported. Allan (1974; reviewed in Forstner and Wittmann 1979) measured the Ni content in sediments collected at the deepest spot in each of a number of lakes within about a 100 km radius of Sudbury. In all cases, the upper 5 cm had the highest Ni concentration, while the deeper layers (10-30 cm below the sediment-water interface) typically had concentrations 2-200 times lower than the surface values.

Scheider et al. (1975) studied the Ni, Cu and pH profiles at several sites in each of Middle, Hannah, Lohi and Clearwater Lakes. Elevated Cu and Ni levels were observed in the upper strata of all lakes (usually the top 4-8 cm; 8-16 cm in Hannah Lake) compared to levels measured in deeper strata. Another study investigated the Cu, Ni and Zn content of the surface layer of sediments from ~200 lakes near Sudbury, (Anon. 1978). However, because the sampling was carried out by Ekman dredge rather than by coring, the quantitative increases could not be evaluated. A strong pattern of increasing Cu and Ni with decreasing distance from Sudbury was evident. On the other hand, the Zn content of the surficial sediments did not form a distinct pattern, suggesting that localized geochemistry or a different atmospheric deposition pattern from that of Cu and Ni was the controlling factor (in accord with conclusions in Chapter 2). No attempts were made to ascertain either the cause or the chronology of the elevated levels of the metals in the sediments.

The noble metal contents of Kelly Lake sediments (situated in the city of Sudbury) were determined by Crocket and Teruta (1976), and compared to particulate emissions from the Copper Cliff smelter. Extremely high levels of Pt, Pd, Au and Ir were found in both sediments and stack emissions. Copper and Ni sediment concentrations were similar to those reported in other studies described previously.

In a more detailed study of 2 lakes in the Sudbury area, Huhn (1974) measured or calculated the sedimentation rate at one site in each lake. Loon Lake, a meromictic lake 51 km N.W. of Sudbury, had visibly countable annual laminae. The calculated sedimentation rate of Loon Lake (~2-3 mm yr^{-1}) was used to determine the sedimentation rate of a second lake (unnamed, 27 km N.E. of Sudbury) by correlation of pollen and smoke microspherule (iron oxide particle) profiles between lakes. This correlation required several assumptions: comparable inputs of pollen and microspherules to the two lakes, equal mixing rates of the surficial sediments by benthic organisms and physical processes, and similar plant species in each lake's vicinity. Huhn found that increases in the microspherule content of each lake roughly coincided with increases in copper and nickel concentrations and with changes in the local vegetation, as evidenced by pollen accumulation. Having assumed that increases in microspherule and metal concentrations resulted from smelter activity, the changes in vegetation were likewise related to acidification of the surrounding terrain. The greatest change observed was the decline in white pine (*Pinus strobus*) pollen.

Walsh (1977) studied diatom remains in the sediments of Hannah, Middle, Lohi and Clearwater Lakes to determine if diatom biomass and species composition were related to the acidification of these lakes. A single ^{210}Pb profile of the top 6 cm of one Hannah Lake core provided a calculated sedimentation rate of 0.8 mm yr^{-1} in the upper 3 cm (Fig. A4-1, Appendix 4), but the interpretation is ambiguous because of the shortness of the core. Dating of the same core using the *Ambrosia* horizon gave a comparable sedimentation rate (0.93 mm yr^{-1}); however, Huhn (1974) had used a date of 1835-40 for the *Ambrosia* horizon in the Sudbury area whereas Walsh used 1883 for the same horizon. Furthermore, the ^{210}Pb profile showed that there was a mixed zone from at least 2 cm to 6 cm below the sediment-water interface, but this mixed zone is not evident in the pollen profiles, suggesting that one or the other is in error. In fact, because mixed zones and site specificity were not considered, and because the chronology was established on the sediments of only one of the 4 study lakes, the conclusions drawn must be considered as qualitative. Walsh found that, while the total biomass of diatoms did not change significantly with depth (ie. with time before the present) in any of the lakes, diatom genera that favored alkaline conditions or were at least indifferent to acidic conditions generally occurred at depths >10 cm below the sediment-water interface. Those diatom genera favoring acidic conditions predominated in the upper 10 cm of the sediments of the 4 lakes, which was considered to correspond to approximately the last ~100 years. On the other hand, a decrease in pH (<5.0) of the sediments in Clearwater Lake, the only chemically untreated lake considered in Walsh's study, was observed in the top 2 cm of one core, but in the top 16 cm of the second core (Fig. A4-2, Appendix 4). No pH reduction was observed in the surficial sediments of the 3 neutralized lakes, a finding supporting the observation of Scheider _et_ _al_. (1975) that the chemical treatment "re-neutralized" the acidic lakes' surficial sediments. The surface sediment pH apparently reflects current chemical conditions in the lakewater rather than historic events, as evidenced by the ease with which the sediment pH is changed and by the lack of correlation between diatom genera changes and pH changes in the same core.

C. Sediment Chronology and Sedimentation Rates

The simplest and undoubtedly most accurate method of establishing the chronology of a lake's sediments is the counting and measurement of annual laminations. However, these laminations occur only in lakes in which the sediments are not mixed a) by physical processes resulting from water movement above the sediments, b) by gas evolution within the sediments, or c) by biological processes, particularly mixing by benthic organisms. Non-mixed conditions exist in very few lakes, usually only those that are meromictic (ie. in which permanent lake stratification occurs).

Other frequently used methods rely on the measurement of substances whose times of introduction into and disappearance from the environment can be established. Pollen, usually _Ambrosia_ or _Castatanea_, the former appearing in a region following the clearing of forested land and the latter disappearing following introduction of chestnut blight, is the most frequent choice (Kemp _et al_. 1976), although iron oxide microspherules resulting from industrial operations (Huhn 1974), volcanic ash (Kimmel 1978) and charcoal produced by forest fires (Swain 1973) have also been used. More recently, radionucleides produced by nuclear reactions have been used as markers in lake sediments (Krishnaswami and Lal 1978). ^{137}Cs, which was first produced in the 1950's by U-235 fission, has been used frequently to date sediments (Pennington 1973). The peaks in the ^{137}Cs profile of a lake's sediments can be matched to the dates of the peaks in the global ^{137}Cs production rates. However, because Cs may be relatively easily mobilized from the watershed to the lake (Ritchie _et al_. 1974) and may diffuse through the interstitial waters of the sediments, interpretation of the ^{137}Cs profile is often ambiguous. Mixing of the upper (most recent) strata by physical or biological processes is a problem inherent to all of these dating techniques. If the sediments are mixed following their deposition, then the marker will be spread over deeper (ie. older) sediments, and if the mixing depth is unknown, the chronologies established will be incorrect. Although this problem is critical, it is often ignored in paleolimnological studies.

Problems relating to sediment mixing are at least partially resolved by the use of naturally occurring radionucleides as dating tools. ^{14}C, produced in the upper atmosphere by cosmic rays, has been used (Likens and Davis 1975), but because of the length of its half-life (5730 years), it is only useful for dating sediments with a resolution of 100's or even 1000's of years. ^{228}Th has been recently used, but its short half-life (1.9 yr) limits its usefulness to the dating of recent sediments which are, of course, those most affected by biological and physical mixing processes (Krishnaswami and Lal 1978).

In order to establish the chronologies of lake sediments over a time scale where effects of recent civilization on aquatic ecosystems might be expected (~10-150 years BP), ^{210}Pb (half-life ~22.3 yr) has been shown to be very useful. The rationale for its use has been reviewed by Koide et al. (1973), Robbins (1978) and Krishnaswami and Lal (1978).

^{210}Pb is an intermediate product of the ^{238}U decay series (Fig. 3-1). It is introduced into lakes' sediments by 2 processes. The decay of ^{226}Ra in the earth's crust results in the exhalation of ^{222}Rn to the atmosphere. This isotope rapidly decays to ^{210}Pb, which is, in turn, rapidly removed by wet precipitation and dry fallout, the mean residence time in the atmosphere being only 5-10 days. The residence time of ^{210}Pb in lakewater is also short because of its affinity for particulates. For the same reason, input of ^{210}Pb to a lake from its watershed is usually negligible unless transport of particulates (erosion) is an important process, which is unlikely in Precambrian areas.

The second process resulting in the accumulation of ^{210}Pb in lake sediments is the decay of the parent ^{226}Ra in the lakewater and sediments themselves. Since the ^{210}Pb produced in this way is in secular equilibrium with the ^{226}Ra in the sediments and water column, this additional activity, which is termed the background or supported ^{210}Pb activity, will be constant.

If the flux of ^{210}Pb to the lake's sediments from the atmosphere has been constant and the ^{210}Pb is not mobile in the sediments, then the change of ^{210}Pb concentration in the sediments will be a function of only radioactive decay and/or change in accumulation rate of lake sediments. Therefore, if no change in sedimentation rate has occurred and there are no processes occurring that result in mixing of the surficial sediments, then the activity of ^{210}Pb will be log-linear with depth (ie. with time) until the supported ^{210}Pb level is reached (Fig. 3-2a). A mixing zone in the upper sediments will result in uniform ^{210}Pb activities over this depth (Fig. 3-2b), while a change in sedimentation rate will result in a break in the linear plot (Fig. 3-2c). However, as Jones and Bowser (1978) have cautioned, partial or slow mixing in the surface layers may appear to be a drastically increased sedimentation rate. In all cases, the ^{210}Pb activity should be plotted as a function of cumulative dry weight (or ash weight) to avoid complications resulting from compaction of the deeper (older) sediments (Robbins 1978, Evans and Rigler 1980).

Calculation of the sedimentation rate from the ^{210}Pb profile at a specific location in a lake is outlined below. It must be emphasized that sedimentation rate measurements are site-specific; that is, historical events reflected in the chemistry and biology of the sediments from the same location within the lake can be ascertained, but the sedimentation rate measured at one location cannot be extrapolated to a whole lake basis (e.g. for mass balance calculations), or even to another site within the lake.

Below the mixed layer (if any), the activity of ^{210}Pb is defined by:

$$A(w) = A(m)e^{-\lambda w} + A(s) \qquad (3\text{-}1)$$

where:

A(w) is the ^{210}Pb activity at any depth defined by w where the mixing zone < w < depth of supported ^{210}Pb level,

w is the depth scale measured as cumulative dry weight per unit area

A(m) is the activity of ^{210}Pb at the bottom of the mixing zone (or at the sediment surface if there is no mixing zone)

A(s) is the activity of supported ^{210}Pb

λ is the ^{210}Pb decay constant ($\ln 2/t_{1/2} \simeq 0.0311\ yr^{-1}$)

The slope, k, of the regression of $\ln[A(w)-A(s)]$ on w is related to the accumulation rate of sediments (r in dry weight $area^{-1}$ $time^{-1}$) by the decay constant, :

$$k = \lambda t/w \quad \text{where } r = w/t$$

$$r = \lambda/k \qquad (3\text{-}2)$$

Sedimentation rates of the one or more linear portions of the ^{210}Pb activity-vs cumulative weight (age) plot can be calculated in this way. Any mixing zone in the surficial sediments will be apparent, and any disturbance such as a major storm that resulted in instantaneous sediment mixing at a point in time in an otherwise undisturbed sediment profile will be recognized by a zone of constant ^{210}Pb activity in an otherwise log-linear profile. Examples of all of these phenomena are apparent in cores from the 2 Sudbury area lakes dated by ^{210}Pb.

D. Results

The major sediment sampling effort was directed to Lohi and Clearwater Lakes. Sediment cores were collected at 5 locations in each of these 2 lakes in 1979 (Fig. A2b-2 and -3, Appendix 2) and the chronology (depth-time relationship) estimated for each core. Although 1 or more cores were collected from the other study lakes, no chronologies were established; some of these results are, therefore, qualitative rather than quantitative.

i. Clearwater and Lohi Lakes

a) Sedimentation Rates

Sedimentation rates were measured at all 5 locations sampled in 1979 in each of Lohi and Clearwater Lakes using the ^{210}Pb methodology. ^{210}Pb profiles and corresponding sediment chronologies are illustrated for one site in each lake in Fig. 3-3 and 3-4, respectively. The cores from these 2 sites are representative of the 5 cores taken within each lake, and are discussed in detail to illustrate the findings.

At the deepest station in Lohi Lake (Core #2), the following is evident: a) the sediments are undisturbed; that is, there is no mixing zone; b) the sedimentation rate increased drastically about 40-45 years ago from an input rate of ~10.0 mg cm^{-2} yr^{-1}, which is typical of Precambrian lakes in southern Ontario (Evans and Rigler 1980b, Dillon unpub. studies), to 38.4 mg cm^{-2} yr^{-1} for a period of about 25 years, then decreased to the earlier levels (8.4 mg cm^{-2} yr^{-1}). Kipphut (1979) has demonstrated that typical confidence intervals for ^{210}Pb chronology are of the order of ±10% meaning that the sedimentation rate change occurred ~42 ± 5 yr BP (1937 ± 5 yr.). This date is consistent with the introduction of the 200 m stacks at Copper Cliff (mid 1930's) and rapidly increasing Ni production at Sudbury. Increasing inputs of strong acid to the lake's watershed probably occured from increased frequency of SO_2 fumigation, and resulted in loss of vegetation, followed by increased leaching and erosion of the overburden in the vicinity of Lohi Lake. This in turn resulted in an increased sedimentation rate.

In contrast to Lohi Lake, the core from the deep station in Clearwater Lake (Core #4, Fig. 3-4) shows a mixed zone that includes the top 0.2 g cm^{-2} (3 cm) of the sediment profile. The ^{210}Pb concentrations actually decrease slightly from the bottom of the mixed zone to the water-sediment interface, probably a result of leaching by the overlying acidic lake water (discussed later). At the deepest station, which should most clearly demonstrate changes in sedimentation rate, an increase of from 5.9 mg cm^{-2} yr^{-1} to 17.3 mg cm^{-2} yr^{-1} occurred about 50 ± 5 years BP (1929 ± 5 yr.). The interpretation of this core's chronology is complicated by the fact that a very recent decline (<20 yr.) in sedimentation rate may be hidden by the mixing zone. An additional uncertainty of several years might, therefore, be expected.

It is possible that the increases in sedimentation rate that occurred 40-50 yr BP in both the Lohi and Clearwater Lake cores actually were greater and more recent than the ^{210}Pb profiles indicate. Because the extra sediment was almost certainly of allochthonous origin (ie. material displaced from the lakes' watersheds), some ^{210}Pb may have been translocated from the watersheds to the lakes' sediments. If this occurred, then the real sedimentation rate during this period when erosion was great was even higher than the 38.4 and 17.3 mg cm^{-2} yr^{-1} calculated from Lohi and Clearwater Lakes, respectively. As a consequence, the date of this increase may be more recent than suggested above. An upper estimate for this potential error is ~10-15 years.

^{210}Pb profiles and sedimentation rate calculations for the remaining 4 cores from each lake are shown in Appendix 4 (Fig. A4-3, A4-4). All of the cores collected from the hypolimnetic sediments of Lohi Lake (#3, 4, 5 as well as #2) have low sedimentation rates, ranging from 5 to 10 mg cm^{-2} yr^{-1} in the deeper sediments, corresponding to a period of from 40-60 yr BP and older. In each case, sedimentation rate then increased as it did in core #2, typically by a factor of 2 to 4. Most of the cores had no mixed zone near the surface, although in 2 cores (#1 and #5), a disturbance resulting in mixing was observed at 30-40 yr BP. One core (#1) collected from epilimnetic sediments, demonstrated a relatively high sedimentation rate (20-25 mg cm^{-2} yr^{-1}) throughout. This core also had no mixing zone, probably because the density of the substrate was at least 2-fold greater than at any other location, the coarse sand likely reducing physical mixing and bioturbation. There is much uncertainty about the interpretation of

^{210}Pb profiles measured in coarse-grained epilimnetic sediments (Evans 1980).

The ^{210}Pb sediment profiles in the additional Clearwater Lake cores (#2, 3, 5), collected in hypolimnetic sediments, all had mixing depths, some of up to 6 cm. In cores #2 and #3, the mixing zones were deep enough to destroy any record of recent sedimentation rate changes. Core #5 also demonstrated disturbances in the upper zone. In all 3 cores, the sedimentation rate at depth was typical of Precambrian lakes (5.6-10 mg cm^{-2} yr^{-1}). All hypolimnetic cores had lower ^{210}Pb concentrations at the sediment-water interface than at greater depth in the core, again suggesting dissolution by the overlying acidic water. The single core collected in the epilimnetic sediments, like that in Lohi Lake, was much denser and had no mixing zone and a higher apparent sedimentation rate (28.8 mg cm^{-2} yr^{-1}) than elsewhere in the lake.

b) Concentration and Deposition of Metals

Profiles of the concentrations of Cu, Ni, Zn, Fe, Pb, Cd and Al at the 5 sampling locations in each of Lohi and Clearwater Lakes are summarized in Appendix 4 (Fig. A4-5, 6). Using chronologies derived from the sedimentation rates measured by the ^{210}Pb method, the measured metal content may be plotted as a function of time (illustrated for Lohi core #2, Clearwater core #4 in Fig. 3-5 a-d and 3-6 a-d, respectively).

In Lohi Lake core #2, the upper 1.0 g cm^{-2} of sediment, corresponding to the top 7 cm or the most recent ~ 50 yr., has extremely high levels of Cu, Pb and Ni, elevated Cd, Zn and Fe, and reduced Al levels, compared to the deeper sediments. Because Fe is mobile in reducing (anoxic) sediments, the Fe profiles may not necessarily indicate increased inputs to the lake. No major changes in the very recent (top-most) sediments, that might be attributable to the neutralization treatments of Lohi Lake, are evident. This may be a result of the re-acidification of Lohi Lake, which was virtually complete by the time these cores were taken (ie. 1979). If the deep layers of the sediments where concentrations are relatively constant are considered to represent background levels, then the peak concentrations in recent sediments were ~40, 40, 3.5, 30, 10 and 2.8 times greater for Cu, Ni, Zn, Pb, Cd and Fe, respectively. The Al levels are reduced by ~20%. Large increases in metal concentrations in the surface sediments were also apparent in all other Lohi Lake cores (Table 3-1, Fig. A4-5), but the surface concentrations varied by as much as a factor of 5, demonstrating that spatial variability may be large.

Sediment enrichment factors (SEF) have frequently been used to quantify enrichment in recent sediments (Forstner and Wittmann 1979, Kemp et al. 1976). However, the elemental changes are usually calculated relative to a "conservative" substance, usually Al, which is considered to reflect non-anthropogenic inputs. The decrease in Al in recent sediments in Lohi Lake, as a result of the acidity of the lake water and sediments, precludes calculation of SEF's for Lohi or Clearwater Lakes. Furthermore, as Evans (unpub. manus.) has pointed out and as the results for the 5 Lohi Lake cores demonstrate, enrichment factors are site-specific within a lake and, therefore, provide limited information. The enrichment factor for Pb in Bob Lake, for example, varied from 2.6 to 27, depending on sampling location (Evans 1980).

Table 3-1. Peak metal concentrations in recently deposited sediments, background levels and ratio of peak to background concentrations for Lohi Lake sediment cores. Bracketed Al concentrations correspond to recent low values

		Cu µg/g	Ni µg/g	Zn µg/g	Pb µg/g	Cd µg/g	Al mg/g	Fe mg/g
Core #1	Peak	940	1500	130	110	1.80	(15)	66
	Bkgd	25	40	100	2	0.40	16	14
	Ratio	38	38	1.3	55	4.5	-	4.7
#2	Peak	3200	3700	350	210	6.90	(20)	50
	Bkgd	87	40	99	3	0.65	23	19
	Ratio	37	93	3.5	70	11	-	2.6
#3	Peak	990	1700	130	140	1.70	(16)	87
	Bkgd	41	43	138	4	0.07	24	19
	Ratio	24	40	<1	35	24	-	4.6
#4	Peak	2400	2600	320	160	6.30	(15)	27
	Bkgd	58	83	109	5	0.58	26	18
	Ratio	41	31	2.9	32	11	-	1.5
#5	Peak	1500	2200	210	150	4.00	(19)	31
	Bkgd	73	92	104	9	0.74	23	18
	Ratio	21	24	2.0	17	5.4	-	1.7
Average Ratio		32	45	2.4	42	11		3.0

The increase in deposition of Cu, Ni, Zn, Fe and Cd began about 50-60 years BP. Because of the possibility of translocation of ^{210}Pb from the watershed of Lohi Lake, this estimate should be considered an upper boundary. Slight elevations of Cu and Ni are evident earlier, but these increases are small. The deposition of all 5 metals increased simultaneously, these increases in deposition corresponding with the increases in atmospheric emissions by the smelter at Copper Cliff. Deposition within the lake into the sediments was probably proportional to deposition from the atmosphere to the lake until the lake acidified. At this point, a decreasing proportion of the input would have reached the sediments, as the acidification of the lakewater kept a greater proportion of the metal in soluble form. On the other hand, the acidification of the watershed probably resulted in a greater transport of the trace metals deposited on the watershed to the lake. Therefore, the sediment deposition record cannot be used to reconstruct an absolute record of atmospheric deposition since the efficiency of the lakes and watersheds as sinks for the metals has not been constant.

Pb elevations apparently began as early as 80-110 years BP, although the increases were very small until 50-60 years BP. The date and pattern of increased Pb concentrations are consistent with those measured in other lakes in north-eastern North-America. These cases have been attributed to long-range transport of Pb introduced into the atmosphere by the combustion of fossil fuels, primarily gasoline (Edgington and Robbins 1975). The potential emissions of Pb into the atmosphere in North America are shown in Fig. 3-7.

Al, like Fe, is a major component of lake sediments. The decrease in Al content of the sediments deposited in the past 50-60

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	Bkgd	87	40	99	3	0.65	23	19
	Ratio	37	93	3.5	70	11	-	2.6
#3	Peak	990	1700	130	140	1.70	(16)	87
	Bkgd	41	43	138	4	0.07	24	19
	Ratio	24	40	<1	35	24	-	4.6
#4	Peak	2400	2600	320	160	6.30	(15)	27
	Bkgd	58	83	109	5	0.58	26	18
	Ratio	41	31	2.9	32	11	-	1.5
#5	Peak	1500	2200	210	150	4.00	(19)	31
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Al, like Fe, is a major component of lake sediments. The decrease in Al content of the sediments deposited in the past 50-60 years is likely a result of the acidification of the lake which, in turn, acidified the interstitial water of the surficial sediments. This resulted in the leaching of Al from the sediments. Since the export of Al from watersheds increases as the input of strong acid increases (Cronan and Schofield 1979), the sediment profile cannot result from a decrease in total input to the lake.

Metal profiles of the cores collected from Lohi Lake in 1978 and 1976 are shown in Appendix 4 (Fig. A4-7, A4-8). The peak concentrations for these cores fall within the range of those of the 1979 cores. The 1976 core (130 cm long) confirms that background levels were reached within the top 20 cm in all cores from Lohi Lake for every metal with the possible exception of Ni. Even in this case, the difference between Ni levels at 20 cm depth and true background is small (2-fold for 1978 core). The depth at which metal concentrations increased above background levels in the 1978 core occurs within the range found in the 1979 cores (1.2 g cm^{-2} below surface in 1978 vs. 1.0 to 1.5 for 1979 cores), confirming similar deposition rates. Concentration increases occurred somewhat deeper (1.75 g cm^{-2}) in the 1976 core, indicating a higher sedimentation rate or deeper mixing zone for that site. Depths of peak concentrations for the 1976 core (~0.3 g cm^{-2}) were within the range of those for the 1979 cores (0.25 to 0.5 g cm^{-2} below surface). The depth of peak concentrations for the 1978 core (0.2 g cm^{-2} below surface) is marginally shallower than the range for the 1979 cores due to a shallow mixing zone. In summary, the limited information collected in 1976 and 1978 is consistent with the extensive data base of 1979.

The metal accumulations in the sediments of Clearwater Lake

(Fig. 3-6) are similar to those in Lohi Lake. The Cu and Ni content of the surface sediments were typically only about one half that of the Lohi cores, while the Zn, Pb, Fe, Al and Cd levels were very similar. The peak values and ratio of peak/background are shown in Table 3-2. Spatial variability is again illustrated, indicating the site specificity of deposition. The lower Cu and Ni concentrations may be the result of different sedimentation rates or may be only a result of the natural within-lake spatial variability. Deposition of Cu and Ni again apparently increased greatly ~50 yr BP. These elements were associated with increases in Fe and Cd, while the Pb increase was more gradual and began somewhat earlier. As observed in Lohi Lake, the decrease in Al occurred at about the same date as the increase in Cu and Ni deposition.

The metal profiles for the 1978 Clearwater Lake core (Fig. A4-9) had peak and background concentrations comparable to the 1979 cores. Depth of initial increase from background levels (1.8 g cm^{-2}) is close to the low end of the range in the 1979 cores (1.25 to 1.9 g cm^{-2}) and peak concentrations are at the low end of the 1979 range (0.25-0.5 g cm^{-2}).

A summary of the chronology for the major changes in the Lohi and Clearwater sediments based on all cores (details in Appendix A4) is given in Tables 3-3 and 3-4. All the cores support the same conclusions (except those for which the surface mixing zone is too great to allow measurement of recent sedimentation) as Lohi core #2 and Clearwater core #4; that is, that the major elevation of Cu, Ni, Zn, Fe, Cd, Pb and the decrease in Al occurred ~50 yr BP. Smaller increases in some metals, particularly Pb began about the time smelting was first carried out in the Sudbury area (~ 100 years BP).

Table 3-2. Peak metal concentrations in recently deposited sediments, background levels and ratio of peak to background concentrations for Clearwater Lake sediment cores. Bracketed Al concentrations correspond to recent low values.

		Cu µg/g	Ni µg/g	Zn µg/g	Pb µg/g	Cd µg/g	Al mg/g	Fe mg/g
Core#1	Peak	630	1300	96	89	0.90	(12)	83
	Bkgd	37	56	59	4	0.28	27	30
	Ratio	17	23	1.6	22	3.2	-	3
#2	Peak	1700	1600	350	150	6.70	(20)	91
	Bkgd	63	76	145	3	0.96	28	32
	Ratio	27	21	2.4	50	7.0	-	3
#3	Peak	1500	1600	290	160	5.10	(19)	79
	Bkgd	60	60	143	3	0.82	25	27
	Ratio	25	27	2.0	53	6.2	-	3
#4	Peak	2000	1800	390	150	6.20	(15)	34
	Bkgd	83	40	93	3	0.63	21	14
	Ratio	24	45	4.2	50	10	-	2
#5	Peak	620	1300	86	120	0.60	(14)	110
	Bkgd	38	40	108	4	0.73	24	21
	Ratio	16	33	<1.0	30	<1.0	-	5
Average ratio		22	30	2.6	41	6.6		3

Table 3-3. The chronology of observed changes in the metal concentrations in cores taken at 5 sites in Lohi Lake. Results expressed at years BP., and are ±15 yr. (estimated).

Observed change	Core Number 1	2	3	4	5
increase in Cu	55	60	50	50	55
increase in Ni	55	60	50	50	55
increase in Zn	55-60	60	–[2]	50	100[3]
increase in Pb	75[1]	110[1]	75[1]	55[1]	60[1]
increase in Cd	–[2]	65	–[2]	50	75[3]
decrease in Al	–[2]	–[2]	50	30	60[3]
increase in Fe	55-60	60	40[3]	50	45

[1] change is very gradual and hard to pinpoint
[2] change not observed
[3] less reliable because change is small

Table 3-4. The chronology of observed changes in the metal concentrations in cores taken at 3 sites in Clearwater Lake. Cores #2 and #3 had mixing zones that prohibited reliable establishment of chronology in the past century. Results expressed as year BP. (±15 yr.).

	Core number		
Observed change	1	4	5
increase in Cu	60	50	60
increase in Ni	60	50	50
increase in Zn	60	50	55[1]
increase in Pb	60	50	60
increase in Cd	50	45	-[2]
decrease in Al	-[2]	35	-[2]
increase in Fe	50	50	50

[1] decline in concentration
[2] change not observed

Also clearly demonstrated by all the cores from Clearwater Lake is the fact that Cu, Ni, Zn, Cd and Pb are found at lower concentrations in the surface 1-2 cm (0 - 0.5 g cm^{-2}) of the hypolimnetic sediments than immediately below this level. The same is true for Cu, Zn, Cd and, in some cores, Ni and Pb for Lohi Lake. Although this might be assumed to indicate either a decrease in input of metals, a decreased sedimentation rate of the metals, or increased leaching from the sediments, it will be shown in subsequent sections that the latter explanation is correct.

c) Nutrients

The total phosphorus (TP) and total nitrogen (TN) content of the Lohi core 2 and Clearwater core 4 sediments are shown in Fig. 3-8 and 3-9, respectively.

In Clearwater Lake, the TP concentration began to drop 35-40 yr BP to a current level of <1/2 that of pre-1940. This TP pattern (Appendix 4) was consistent in all but the one of the 1979 cores, which was the only core taken from the littoral area of Clearwater Lake. There was a corresponding, but much smaller decline, in TN content. However, the TN pattern was less consistent, with evidence of a decrease in recent sediments apparent in only some of the cores.

Plots of the cumulative content vs cumulative dry weight (Fig. 3-10) decrease the short-term variability (ie. noise) and show general trends more clearly. A straight-line plot indicates a uniform content throughout the core. Curvature in the plots for the near surface portion of the cores suggests that a small decrease in TN accumulation rate and a greater decrease in the rate of TP accumulation occurred, beginning about 40 yr BP in Clearwater Lake.

Comparable results were found in Lohi Lake (for example, core #2; Fig. 3-11). The total phosphorus content was lower in recent sediments in all but one littoral zone core, while TN was slightly less in the top layers of some cores. These changes correspond to sediments of 40-45 yr BP. A very recent increase in TP and particularly in TN in the upper 0.1-0.3 g cm^{-2} may reflect neutralization treatment.

There are several possible explanations for the lower TP and TN content of the recent sediments: a) these elements, like several of the metals (including ^{210}Pb) have been leached from the sediments by the overlying acidic water, i.e. the sedimentation rate is not different from historical levels, b) the actual sedimentation rate, particularly of TP, may have been reduced because of reduced input or loading to the lake and/or reduced incorporation of the TP load into the biota by primary production, or c) a constant sedimentation rate of nutrients in organic matter may have been associated with an increased sedimentation rate of material that was not produced by primary production, eg. clays, sands, etc., from the watershed.

Although it is impossible to unequivocally resolve this problem with the information available, some observations can be made. Although in Clearwater Lake core #4, the metals are reduced in the recent sediments, they are not reduced in a similar core from Lohi Lake (#2). However, there are comparable TP decreases in both lakes. It is likely that mobile metals such as Zn and Cu would be leached from surface sediments before the TP content would be affected. Therefore, the hypothesis that TP has been leached from the recent sediments is not supported.

Loss-on-ignition (LOI) is a measure of the organic content of the sediments. A decline in LOI comparable to TP in the sediments of the past 35 yrs. has occurred in Lohi Lake and Clearwater Lake (Fig. 3-12 and 3-13, respectively). The decrease in organic matter content also is inconsistent with hypothesis "a" above, but supports hypothesis "b", since under acidic conditions respiration is probably reduced (Chapter 1).

The Lohi Lake data support the possibility that increased sedimentation rate is at least partially responsible for the lower TP and TN content in recent sediments. The increased rate probably resulted from a period of increased erosion as the watersheds were acidified. If the cumulative TP content $(\text{area})^{-1}$ is normalized against time (yr BP, Fig. 3-14), it is seen that there was a great increase in TP accumulating per unit time between 45 and 25 yr BP, despite the fact that the TP concentration was decreasing. Therefore, increased sedimentation rate of material of non-biologic origin is partially responsible for the decrease in TP concentration. However, the most recent sedimentation rate (from 25 yr BP to the present) is not significantly different from that of >45 yr BP, yet the TP concentration is ~50% as great. The uppermost region of Fig. 3-14 shows that TP is accumulating at the slowest rate of any time in the past 200 years. This indicates that additional sedimentation of inorganic (probably allochthonous) material cannot fully explain the reduced concentrations and that a reduced TP load and/or reduction in biological uptake and settling has also occurred.

In Clearwater Lake core #4, the mixing zone may mask very recent changes in sedimentation rate. However, the 3-fold change in total sedimentation rate that occurred ~50 yr BP (Fig. 3-4) accounts for the decrease in TP concentrations and in increased TP accumulation rate. Other cores with reduced TP concentration in the last 50 years, (#5, Fig. A4-7b), however, do not have an increased total sedimentation rate to account for the TP reduction.

ii. Hannah and Middle Lakes

a) Concentrations of Metals

Metal profiles for Hannah and Middle Lake sediments, measured several years following the neutralization and the fertilization with phosphorus of each lake, are shown in Fig. 3-15 and 3-16, respectively. Profiles from single cores collected in 1976 using the piston corer are shown in Appendix 4, Fig. A4-10, 11. These 100-150 cm long cores were used primarily to ascertain background concentrations in the sediments.

The major increases in Cu, Ni, Zn, Pb and Cd concentrations in the Hannah Lake sediments occurred at a depth equivalent to ~1.5 g cm^{-2}. Peak concentrations of Cu and Ni were 140 and 120 times greater than the background level, while peak Zn, Pb, Cd and Fe concentrations were 2-15 times background. These figures are comparable to those measured for Clearwater and Lohi Lakes with the exception of Cu and Ni, both of which are much more elevated in Hannah Lake. Although in-lake spatial variability would possibly account for this, a more probable explanation is the difference in distances of the lakes from the Copper Cliff smelter, a difference that is also manifested in differing atmospheric deposition of the same metals (see Chapter 2).

Beginning at a depth of 0.6 - 1.0 g m^{-2}, the concentrations of metals declined. As in Clearwater Lake, this is probably the result of decreased deposition of metals from the water column to the sediments as a consequence of the increased proportion of metals in soluble form in the acidic lakewater. However, unlike Clearwater Lake, the Hannah Lake sediments have a second peak concentration of Cu, Ni, Zn, Pb and Cd at the sediment-water interface. One possible explanation of this is the instantaneous removal of the metals in the water column at the time of neutralization. The loss in metals stored in the water column following chemical treatment is adequate for explanation of these recent peaks. For example, ~800 µg Cu cm^{-2} were lost from the water column (Appendix 6), but the accumulated recent peak accounts for ~300 µg cm^{-2}. This difference may be attributable to spatial variability in sediment accumulation. A second explanation for the recent peaks is that a return to a sedimentation pattern indicative of the current circum-neutral water chemistry has occurred. It is not possible to determine which of these explanations is valid.

The profiles in Middle Lake are similar to those in Hannah Lake. Major increases in the concentrations of Cu, Ni, Zn, Pb, Cd and Fe occurred at a consistent depth of ~1.25 g cm^{-2}. The concentrations (except for Pb) levelled off at ~0.5 g cm^{-2}, but did not decline as in Hannah Lake, then reached a second peak at the sediment-water interface. As with Hannah Lake, these peaks can be accounted for by instantaneous loss of metals from the water column as a result of the addition of $CaCO_3$ and $Ca(OH)_2$, or by a subsequent increased sedimentation rate of metals following elevation of lake pH.

b) Nutrients

The LOI, TP and TN profiles for Hannah and Middle Lakes are shown in Fig. 3-17 and 3-18, respectively.

In Hannah Lake, organic content, TP and TN concentrations began to decline at the same depth as the increase in metals occurred. Concentrations decreased to ~1/2 that of background at a depth of ~0.25 - 0.5 g cm^{-2}, then rose abruptly at the surface (ie. in the uppermost 1 cm). The increases near the surface are even more recent than those for Cu, Ni and the other metals, suggesting that these resulted from fertilization rather than neutralization.Although an accurate calculation of loss of TP from the water column following neutralization cannot be carried out because of the poor precision of analytical results at the very low levels encountered in the water, the amount accumulated in the upper layer is much greater than the total amount that was in the water column prior to neutralization. In addition, there was no apparent change in TN in the water column following treatment. Although sedimentation rates were not measured, it is probable that treatment with phosphorus increased the rate of TP and TN deposition as well as the concentration in the sediments, since it is likely that total deposition of sediments increased following fertilization. The sharp peaks in LOI, TP and TN in the upper 0.1 g cm^{-2} of sediment (corresponding to the upper 1-cm section) indicate that significant sediment mixing is not occurring.

The profiles of LOI, TN and TP in Middle Lake are very similar to those of Hannah Lake. Peaks at the sediment-water interface cannot be explained on the basis of removal of material from the water column following neutralization. However, they coincide with phosphorus additions, as in Hannah Lake. That these peaks are a result of fertilization is further indicated by the profiles collected in 1976 in each lake (Fig. A4-10, A4-11). At this time, 1 year following the first P additions to Middle Lake and during the first year of P additions to Hannah Lake, there was no indication of any increase in nutrient content of the surface sediments.

The Hannah and Middle Lake profiles indicate that, like Clearwater and Lohi Lakes, the nutrient cycles within these lakes were altered by acidification. Without establishing chronologies, it is not possible to determine exactly how these alterations occurred, eg. from reduced total sedimentation because of decreases in production (ie. particulate matter), or from increased total sedimentation as a result of the erosion of watershed materials with little nutrient content. Following neutralization and particularly fertilization, the sediments' chemistry is approaching that of the pre-acidification period in these lakes.

E. Summary

1. The sedimentation rates of the hypolimnetic sediments of Lohi and Clearwater Lakes increased by 200-400% about 40-50 years BP (before present). Prior to these changes, the sedimentation rates were typical for oligotrophic Precambrian lakes (5-10 mg cm^{-2} yr^{-1}). In cores that had no mixing zone in the upper layers, the sedimentation rates declined to the early levels in approximately the last 2 decades.
2. The concentrations in and deposition rates to the sediments of Cu, Ni and Pb have increased by 1 to 2 orders of magnitude relative to background levels. Cd, Fe and Zn concentrations have also increased, but by lesser amounts (generally 100% to 1 order of magnitude). These increases coincide with a decrease in Al concentration which reflects acidification of the lake. The major changes in Cu, Ni, Cd, Fe, Zn, Pb and Al occurred simultaneously, about 50 ±15 yr BP. These changes coincided with the increased Ni and Cu production at Sudbury, with the Falconbridge Smelter opened in 1929 and the Copper Cliff tall stack (155 m) opened in 1930.
3. The concentration of phosphorus in the sediments of Lohi and Clearwater Lakes decreased ~40-45 yr BP. A small increase in the uppermost layer (~1 cm) in Lohi Lake reflects the effect of the neutralization treatments. The accumulation rates of P increased greatly ~40-45 yr BP, because of the increase in sedimentation rates, then decreased to rates that were lower than those indicated as background rates (>45 yr BP).

4. The concentrations of Cu, Ni, Zn, Pb, Cd and Fe were greater in the upper or recent sediments (~1.5 g cm^{-2}) in Middle and Hannah Lakes than in deep or background sediments, by factors that were comparable to those measured for Clearwater and Lohi Lakes.

5. The organic content (LOI) and phosphorus and nitrogen concentrations of the sediments of Middle and Hannah Lakes decreased at about the same time as the metal concentrations increased. There was a rapid increase in concentration of these 3 parameters in the most recent sediments (~0.1 g cm^{-2}), which is attributable to the neutralization and fertilization treatments of the lakes.

LIST OF FIGURES

Fig. 3-1. The ^{238}U decay series with half-lives of the intermediate (from Kipphut 1979).

Fig. 3-2. Examples of ^{210}Pb profiles.

a) steady accumulation rate with no mixing.

b) steady accumulation rate with surficial mixing zone.

c) faster sedimentation rate in upper sediments or partial or slow mixing of the surface layers (from Jones and Bowser 1978).

Fig. 3-3. Unsupported ^{210}Pb content vs cumulative dry weight per unit area for Lohi Lake core #2. At this location (depth = 17.8 m), the recent sedimentation rate (8.4 mg cm^{-2} yr^{-1}) is comparable to that of >45 years BP (10.6 mg cm^{-2} yr^{-1}), but much less than that of an intermediate 18-year period (38.4 mg cm^{-2} yr^{-1}). There is no apparent mixing zone in the surficial sediments.

Fig. 3-4. Unsupported ^{210}Pb content vs cumulative dry weight per unit area for Clearwater Lake core #4. The mixing zone at site 4 (depth 19.0 m) is much smaller (0.35 g cm^{-2}; 3 cm) and does not obscure the change in sedimentation rate from 5.9 mg cm^{-2} yr^{-1} to 17.3 mg cm^{-2} yr^{-1} which occurred ~50 yr BP.

Fig. 3-5. Heavy metal concentrations vs. cumulative dry weight per unit area for Lohi Lake core #2 with chronologies according to the ^{210}Pb profile (Fig. 3-3).

a) Cu and Ni levels are extremely high at

the sediment-water interface, declining to a low background level at ~1.0 g cm^{-2} below surface or ~55 years BP.

(b Zn and Pb also show elevated concentrations at the surface; Zn declines rapidly to 55 years BP, Pb shows a less steep decline to a background level at around 1.5 g cm^{-2} below surface or ~95 years BP.

c) Cd concentrations are similar in pattern and time to the first three metals with a slight decline in the top 20 years of sediment, possibly due to leaching.

d) Fe levels are highest just below sediment surface, with a small decline in the past 20 years and a sharp decline to steady background levels at 55 yrs. BP. Al levels have been reduced by 20% in recent sediments, probably because of leaching into the acidic lake water.

Fig. 3-6. Heavy metal concentrations vs. cumulative dry weight per unit area for Clearwater Lake sediment core #4, 1979, with chronology according to the ^{210}Pb profile (Fig. 3-4).

a) Cu and Ni deposition increased steadily from about 1.0 g cm^{-2} below surface to near the sediment water interface, with a sharp decline in the most recent sediments.

b) Zn and Pb follow a similar pattern. Zn concentrations in the topmost sediments have dropped as low as background levels. Pb deposition has a more gradual increase from deeper sediments (~ 1.25 g cm^{-2}).

c) Cd concentrations also increased from about 1.0 g cm^{-2} below surface to elevated levels near the surface, and a sharp decline at the surface to background levels.

d) Al levels decrease and Fe increases at chronologies corresponding to the Cu and Ni increases.

Fig. 3-7. Lead production in the U.S.A. (from Chow 1978).

Fig. 3-8. Nutrient concentration vs. cumulative dry weight per unit area and chronology according to the 210-Pb method for Lohi Lake (Fig. 3-3) core #2, 1979.

a) TP concentration in recent sediments is at a minimum, increasing steadily to twice the current level at ~40 yrs BP.

b) TN has a less obvious but similar pattern of lowest values in recent sediments. There is an increase in concentration of TN in the most recent sediments.

Fig. 3-9. Nutrient concentration versus cumulative dry weight per unit area and chronology according to the ^{210}Pb profile (Fig. 3-4) for Clearwater Lake core #4, 1979.

a) TP concentration was at a steady background level until ~55 years BP, from which time it has been declining to a present level of <1/2 background.

b) TN levels also decline in a similar pattern, although the decline is smaller.

Fig. 3-10. Cumulative content per unit area versus cumulative dry weight per unit area for Clearwater Lake core #4, 1979.

a) TP has a high accumulation rate in the deep sediments up to about 0.8 g cm^{-2} or 30 yrs. BP, and a lower rate in the recently deposited sediments.

b) TN has the same pattern, although the difference in the deep and recent accumulation rates is smaller. Similar results occurred in all but the one littoral core from this lake.

Fig. 3-11. Cumulative content of nutrient per unit area vs. cumulative dry weight per unit area for Lohi Lake core #2, 1979.

a) TP accumulation rate began to decline at 0.9 g cm^{-2} (~40-45 yr BP).

b) The TN pattern is similar, but less pronounced.

Fig. 3-12. Loss on ignition versus cumulative dry weight per unit area for Lohi Lake core #2, 1979. A decrease in organic content of the recent sediments can be seen, corresponding in time to the nutrient content decreases (Fig. 3-8).

Fig. 3-13. Loss on ignition versus cumulative dry weight per unit area for Clearwater Lake core #4, 1979. A similar recent decrease in organic content of about 20% from background levels accompanies the nutrient concentration reductions (Fig. 3-9).

Fig. 3-14. Total cumulative phosphorus content per unit area versus time (in years before present) for Lohi Lake

sediment core #2, 1979. Three accumulation rates are apparent, one of 16.8 $\mu g\ cm^{-2}\ yr^{-1}$ in the deep sediments deposited pre-1945, a much higher rate in the years during which the watershed was acidifying and contributing organic material to the lake, and a very low recent rate of 8.9 $\mu g\ cm^{-2}\ yr^{-1}$, indicating a reduction in biological uptake and settling and/or a reduced TP load in the past 25 years when compared to the total sedimentation rates on Fig. 3-3.

Fig. 3-15. Metal concentrations vs. cumulative dry weight per unit area for Hannah Lake sediment core #1, 1978.

a) Cu and Ni concentrations rapidly increase from background levels starting at 1.5 $g\ cm^{-2}$. The concentrations decrease between 0.75 to 0.5 $g\ cm^{-2}$ deep, probably as a result of acidification of the lake. Following neutralization, Cu and Ni again rapidly accumulated in the most recent sediment layer.

b) Zn and Pb follow the same trends as Cu and Ni, although Zn, during the initial acidification of the lake concentrations, dropped to near background levels because of Zn's higher solubility. Pb typically starts to increase in concentration earlier and more gradually than other metals in response to atmospheric deposition from the burning of fossil fuels.

c) Cd concentrations also show the same trends as Cu and Ni as does

d) Fe.

Fig. 3-16. Metal concentrations versus cumulative dry weight per unit area for Middle Lake sediment core #1, 1978.

a) Cu and Ni increase from a steady background level beginning around 1.25 g cm^{-2} deep. Concentrations level off between 0.5 and 0.25 g cm^{-2} deep, then rapidly increase near the surface.

b) Zn and Pb. Zn follows the same patterns, although background concentrations are erratic in comparison with other cores. Pb accumulations are similar to the other metals.

c) Cd concentrations also rapidly increase from 1.25 g cm^{-2}, at 0.5 g cm^{-2} a decline in levels occurs followed by an increase at the surface.

d) Fe concentration follows a similar pattern, although increases and decreases are less pronounced.

Fig. 3-17. Organic content (expressed as LOI) and nutrient concentration versus cumulative dry weight per unit area for Hannah Lake sediment core #1, 1978.

a) Loss-on-ignition rapidly decreased from background between 1.25 and 0.2 g cm^{-2} deep, corresponding to the acidification of Hannah Lake. The most recent sediments have an increase in organic content.

b) TP concentrations also decreased, starting at 1.25 g cm^{-2}, but increased in the very recent sediments.

c) TN concentrations behave similar to TP.

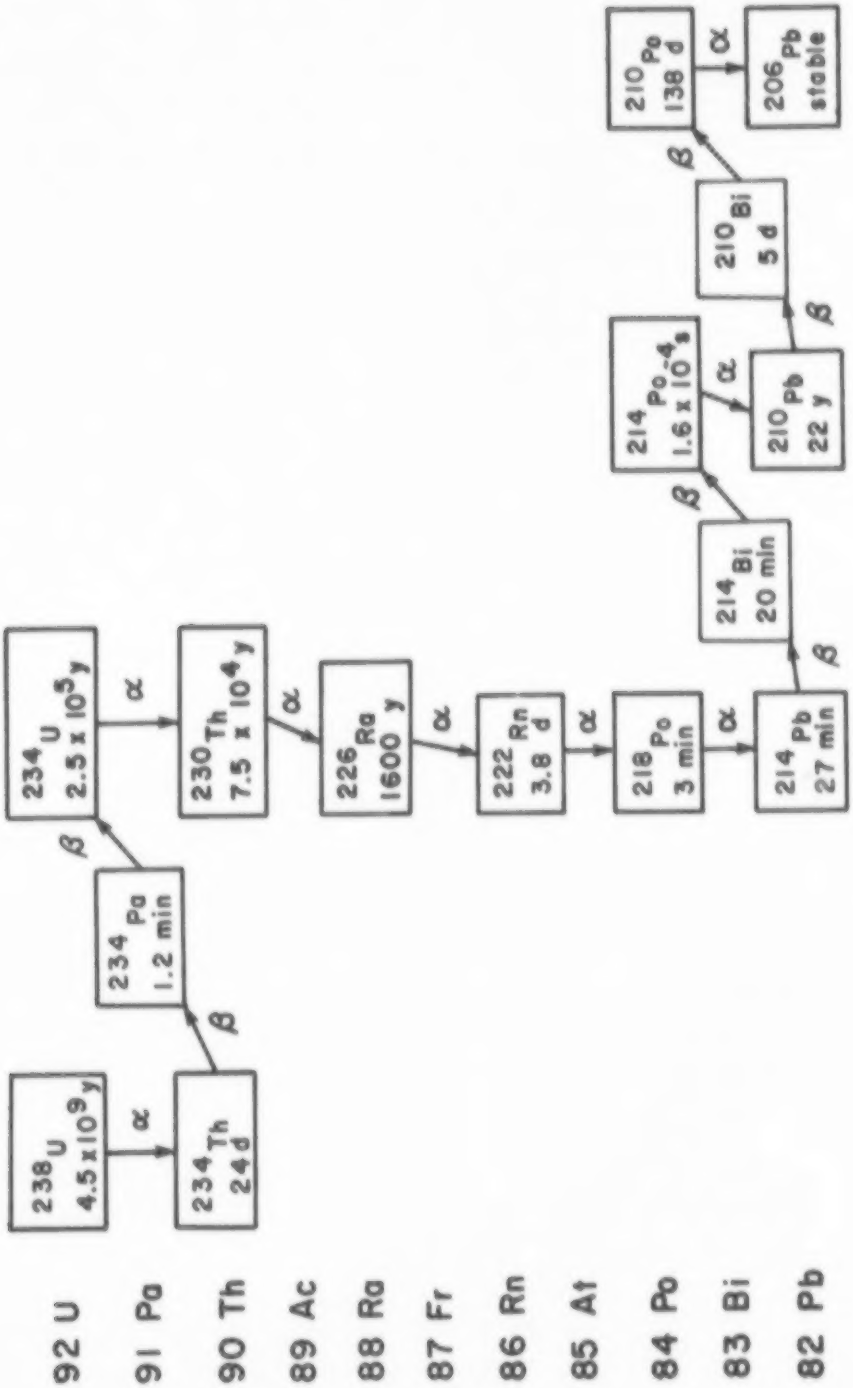
Fig. 3-18. Organic content and nutrient concentrations versus cumulative dry weight per unit area for Middle Lake sediment core #1, 1978.

a) Loss-on-ignition had a steady background level up to 1.0 g cm^{-2} where a rapid decrease in organic content takes place to 0.25 g cm^{-2}. An increased organic content in the most recent sediments is a response to the fertilization of the lake.

b) The TP and

c) TN concentration patterns are similar to LOI, although the recent increase in accumulation rates occurs slightly deeper.

Fig.3-1



92 U
91 Pa
90 Th
89 Ac
88 Ra
87 Fr
86 Rn
85 At
84 Po
83 Bi
82 Pb
238 U 4.5 x 10^9 y
α
234 Th 24 d
β
234 Pa 1.2 min
β
234 U 2.5 x 10^5 y
α
230 Th 7.5 x 10^4 y
α
226 Ra 1600 y
α
222 Rn 3.8 d
α
218 Po 3 min
α
214 Pb 27 min
β
214 Bi 20 min
β
214 Po 1.6 x 10^-4 s
α
210 Pb 22 y
β
210 Bi 5 d
β
210 Po 138 d
α
206 Pb stable

Fig.3-2

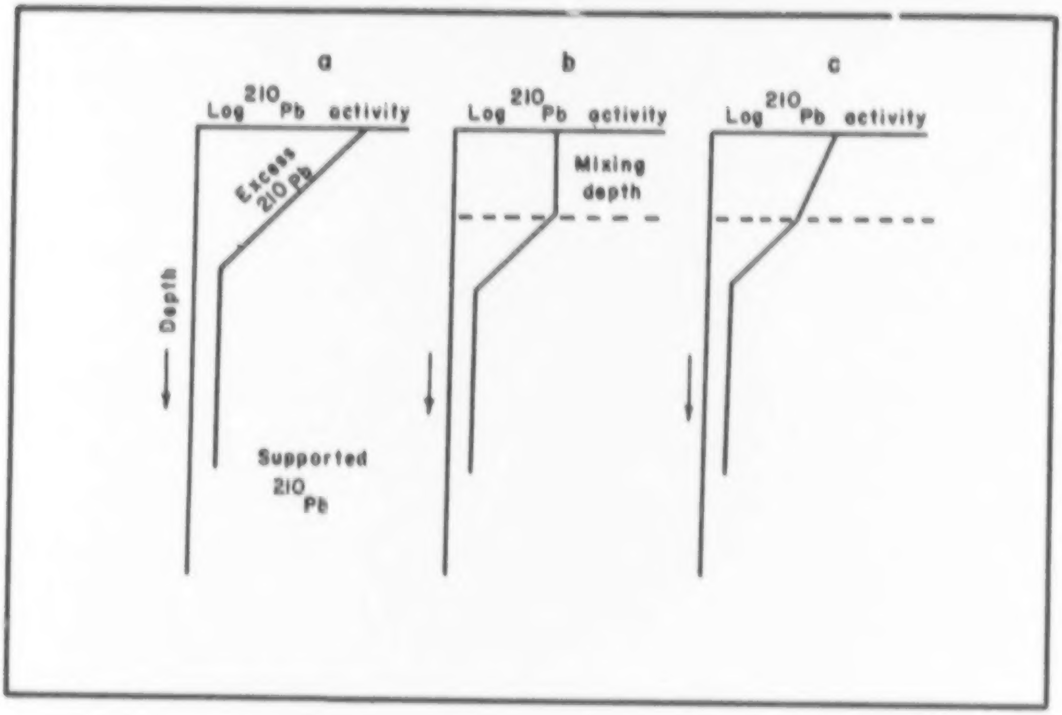
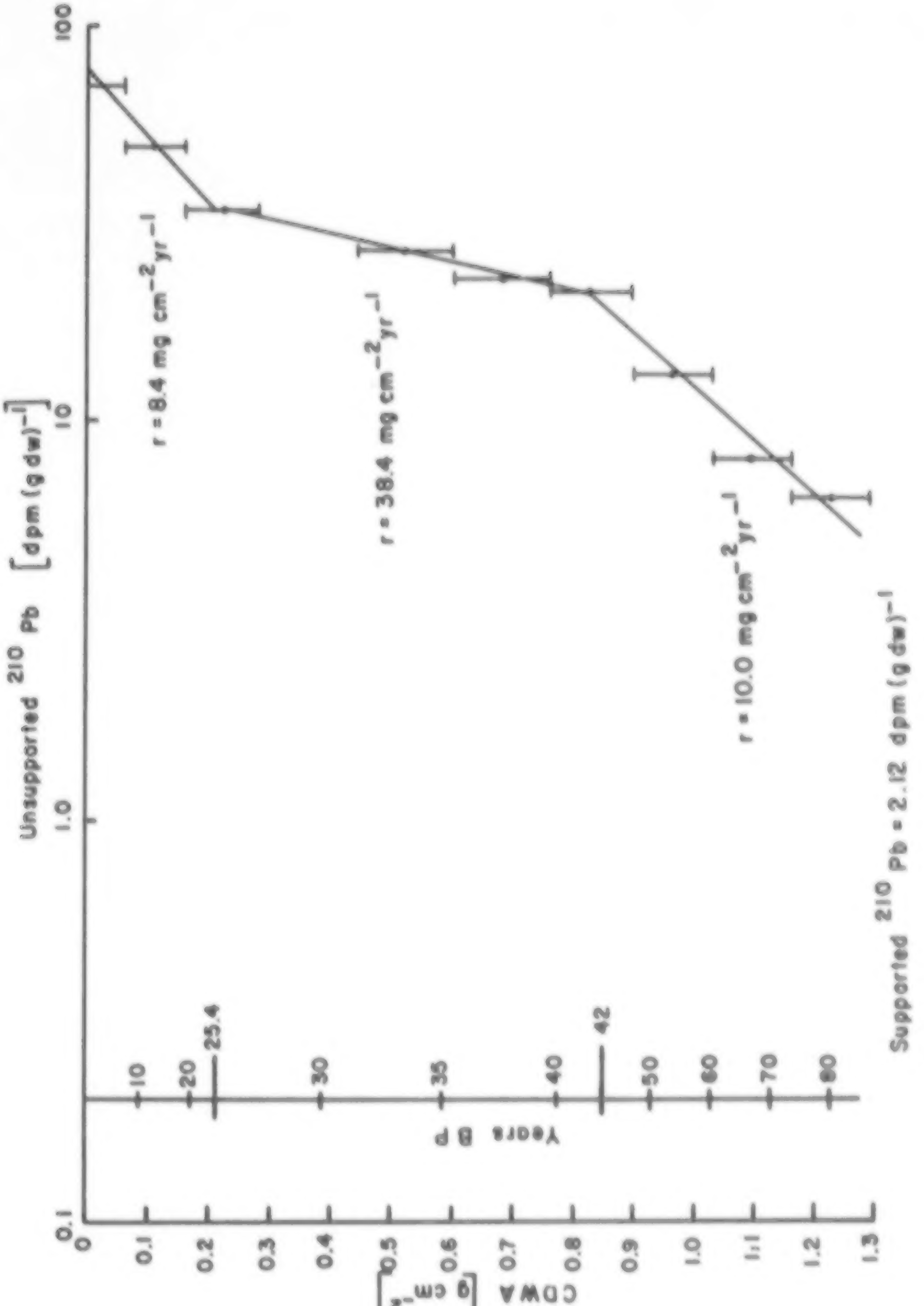
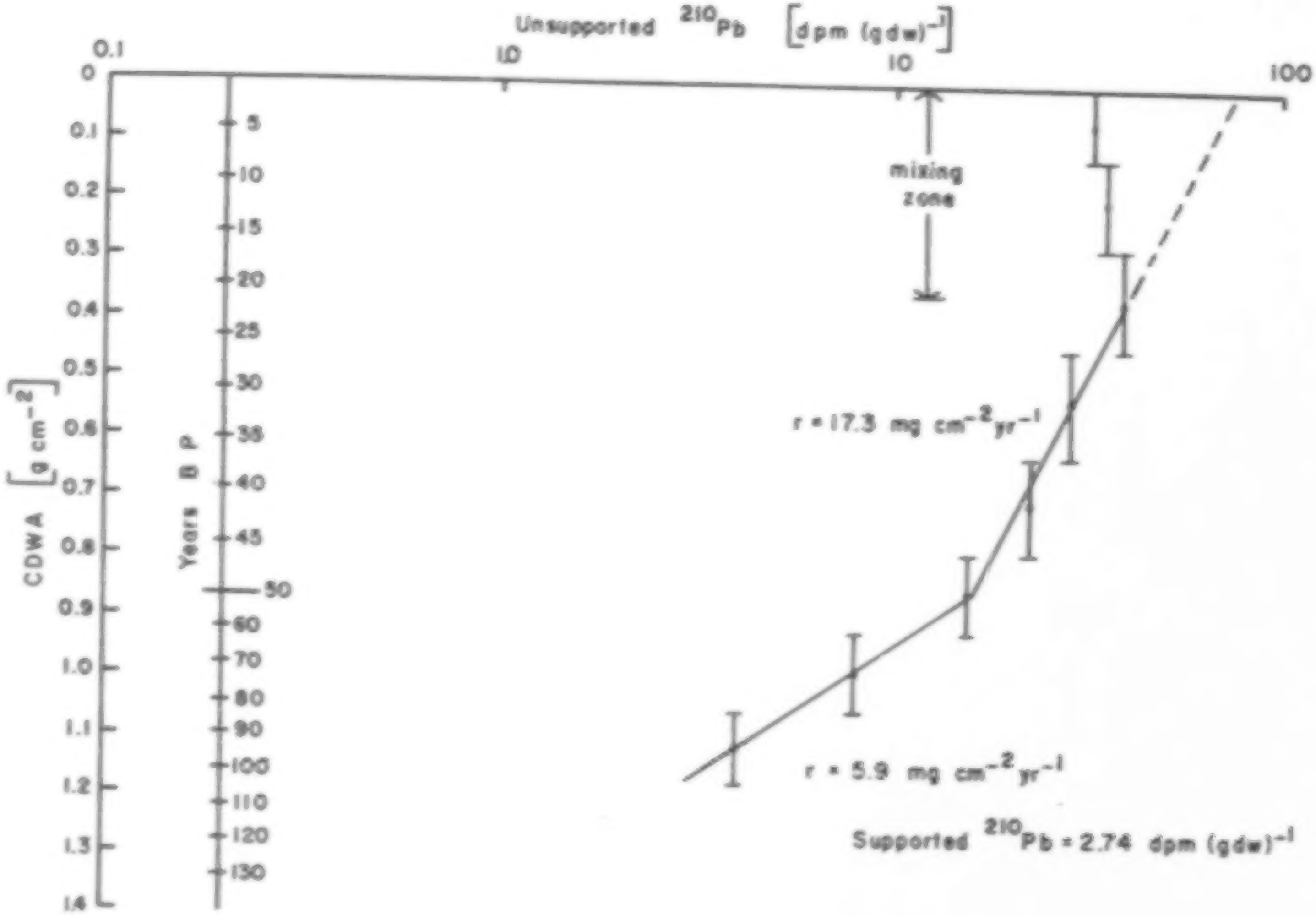

a
b
c
Log ^{210}Pb activity
Log ^{210}Pb activity
Log ^{210}Pb activity
Excess ^{210}Pb
Mixing depth
Depth
Supported ^{210}Pb

Fig.3-3



LOHI LAKE SEDIMENT CORE No. 2 1979

Fig.3-4



CLEARWATER LAKE SEDIMENT No.4 1979

Fig.3-5a

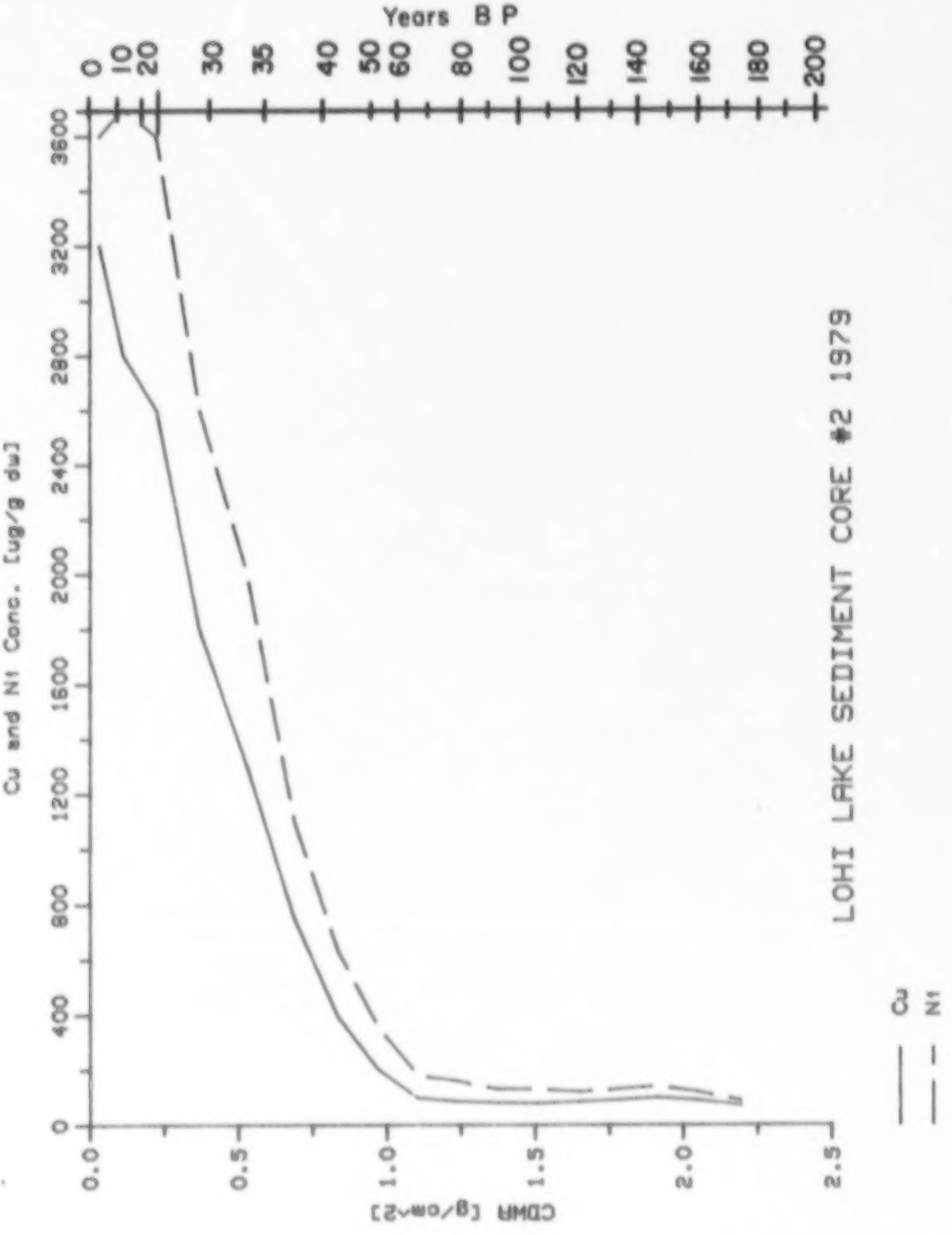

LOHI LAKE SEDIMENT CORE #2 1979
Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
Cu and Ni Conc. [ug/g dw]
0
400
800
1200
1600
2000
2400
2800
3200
3600
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
Cu
Ni

Fig.3-5b

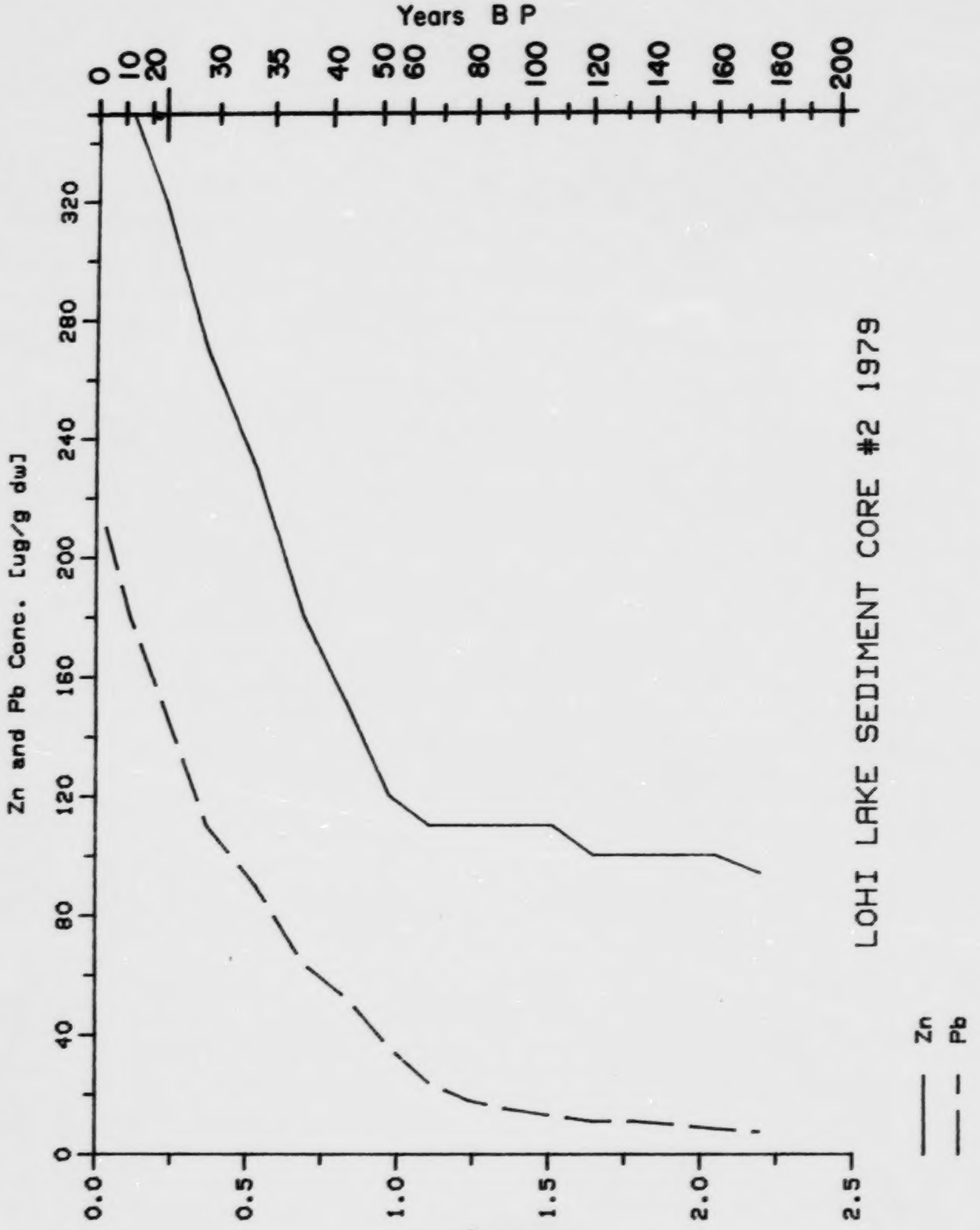

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
Zn and Pb Conc. [ug/g dw]
0
40
80
120
160
200
240
280
320
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2 1979
Zn
Pb

Fig.3-5c

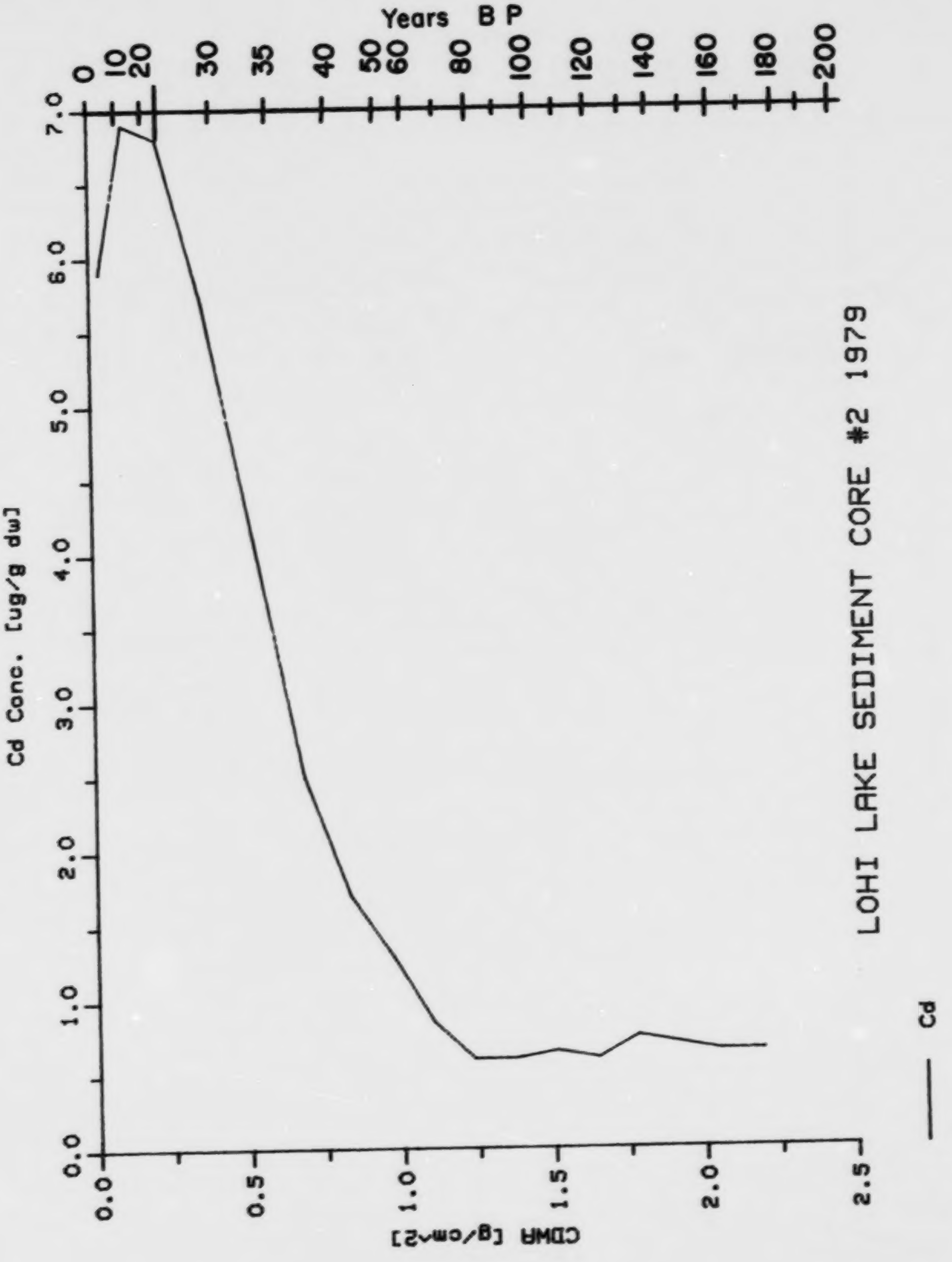
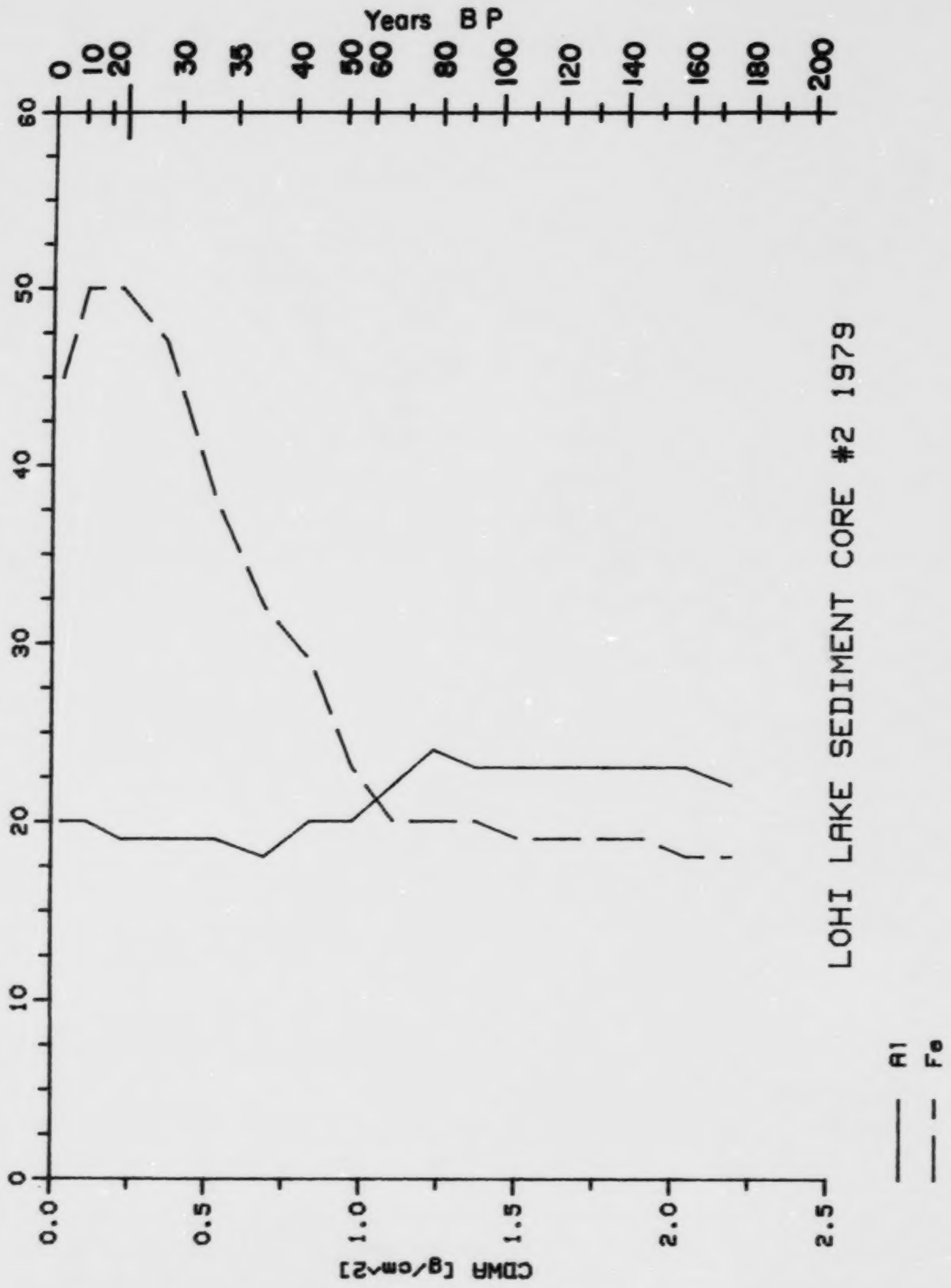
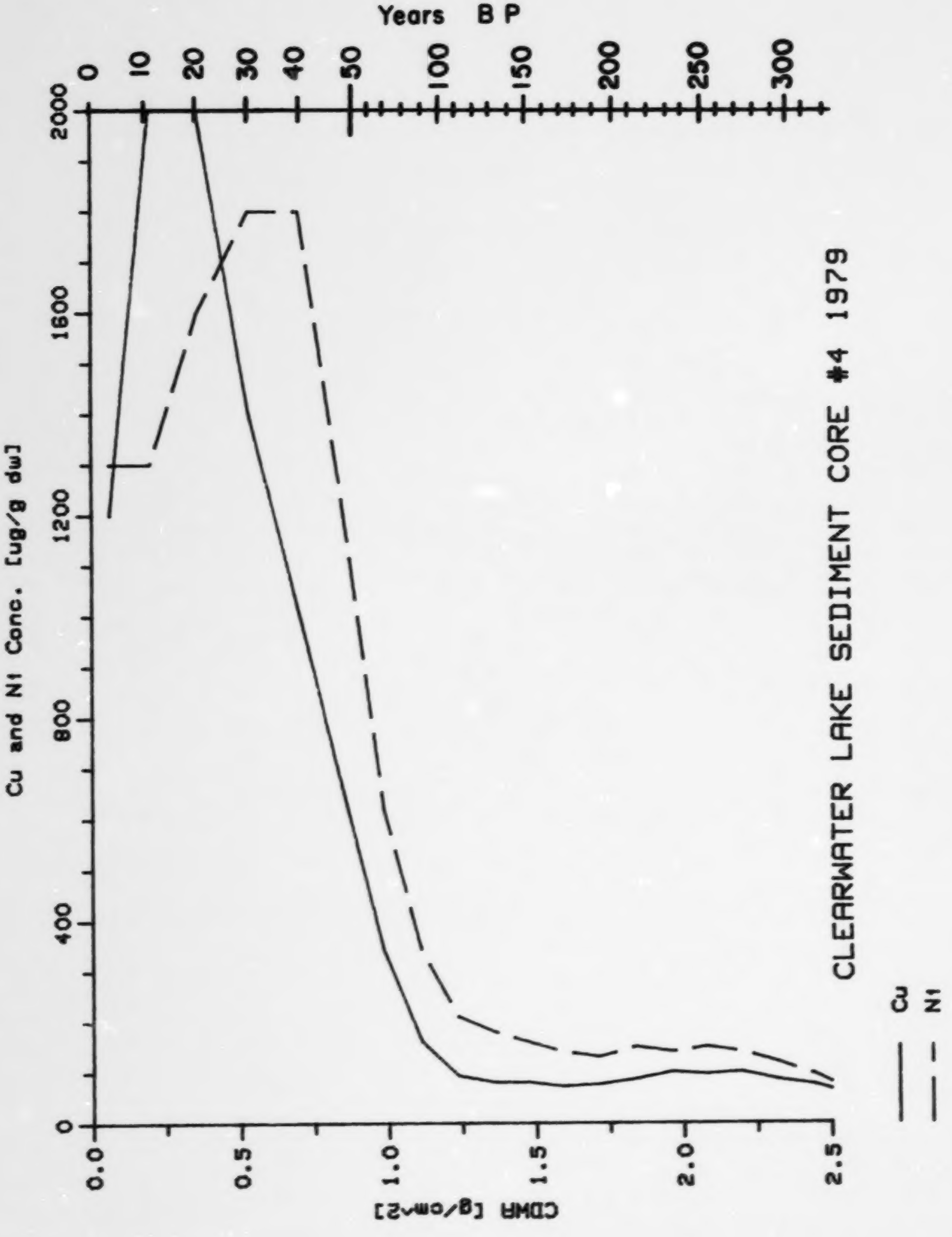

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
Cd Conc. [ug/g dw]
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2 1979
Cd

Fig.3-5d



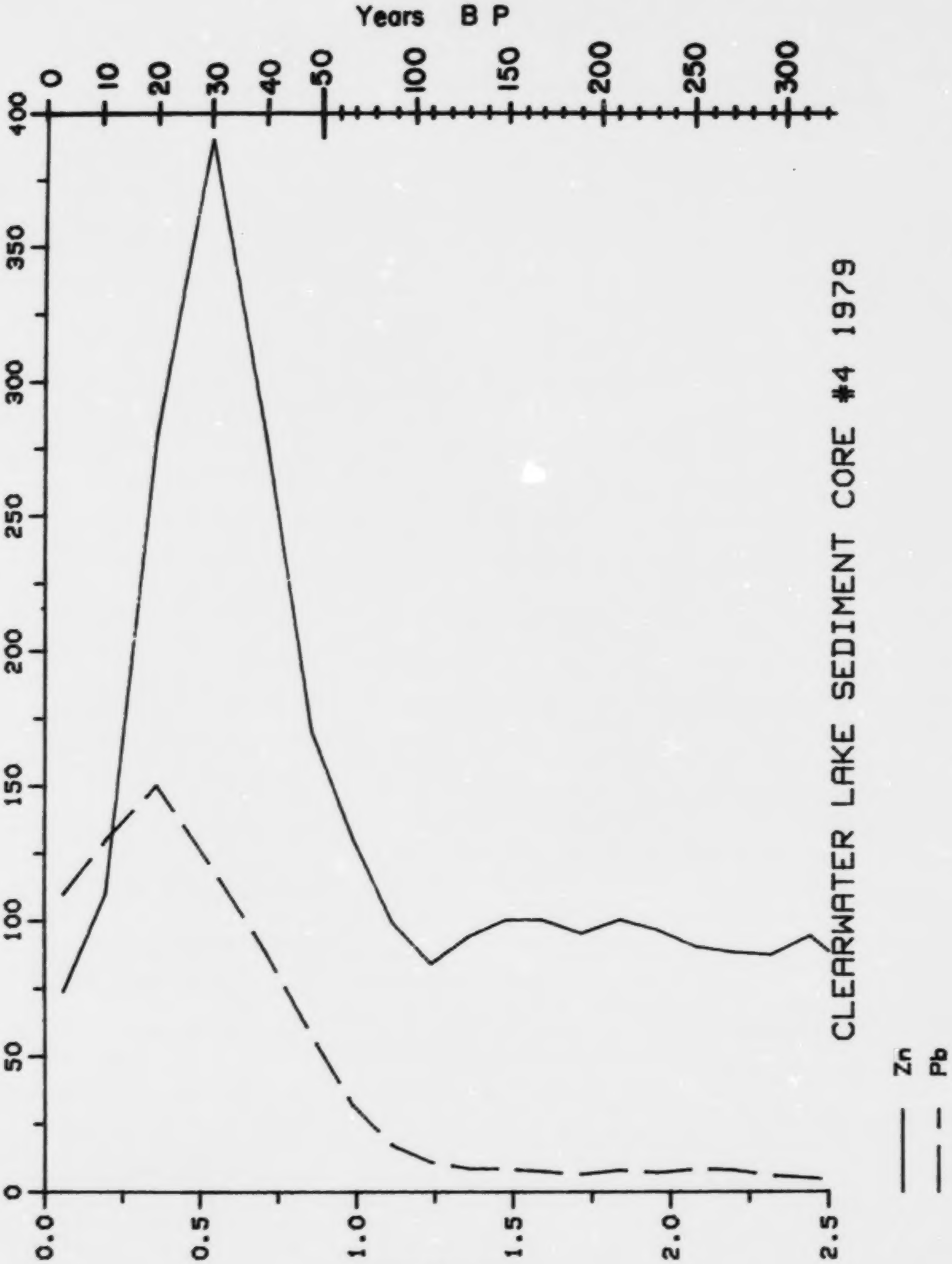
Years BP
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
Al and Fe Conc. [mg/g dw]
0
10
20
30
40
50
60
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2 1979
Al
Fe

Fig.3-6a



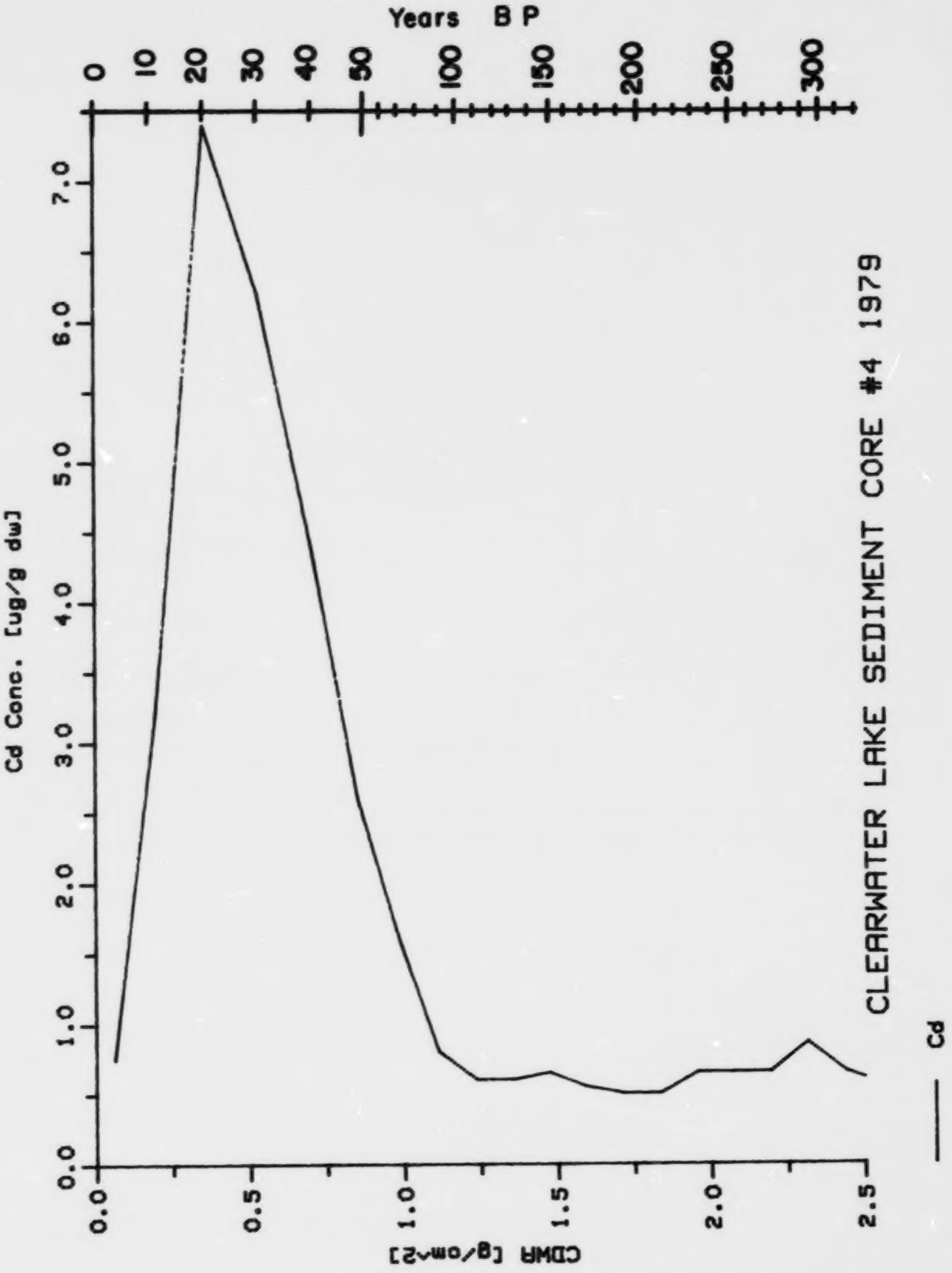
Years B P
0
10
20
30
40
50
100
150
200
250
300
Cu and Ni Conc. [ug/g dw]
0
400
800
1200
1600
2000
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979
Cu
Ni

Fig.3-6b



Years B P
0
10
20
30
40
50
100
150
200
250
300
Zn and Pb Conc. [ug/g dw]
0
50
100
150
200
250
300
350
400
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979
Zn
Pb

Fig.3-6c



CLEARWATER LAKE SEDIMENT CORE #4 1979
Years BP
0
10
20
30
40
50
100
150
200
250
300
Cd Conc. [ug/g dw]
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
Cd

Fig.3-6d

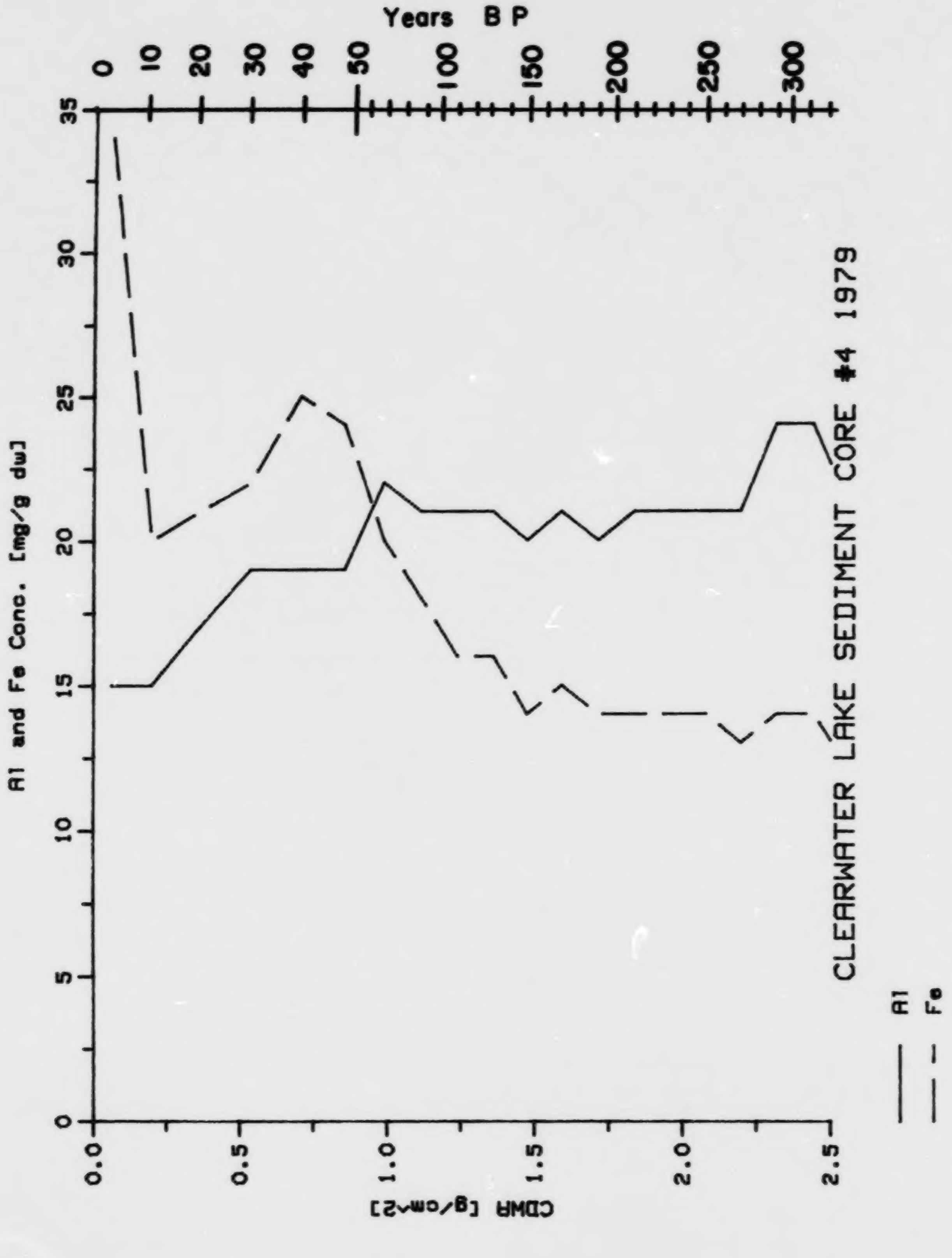
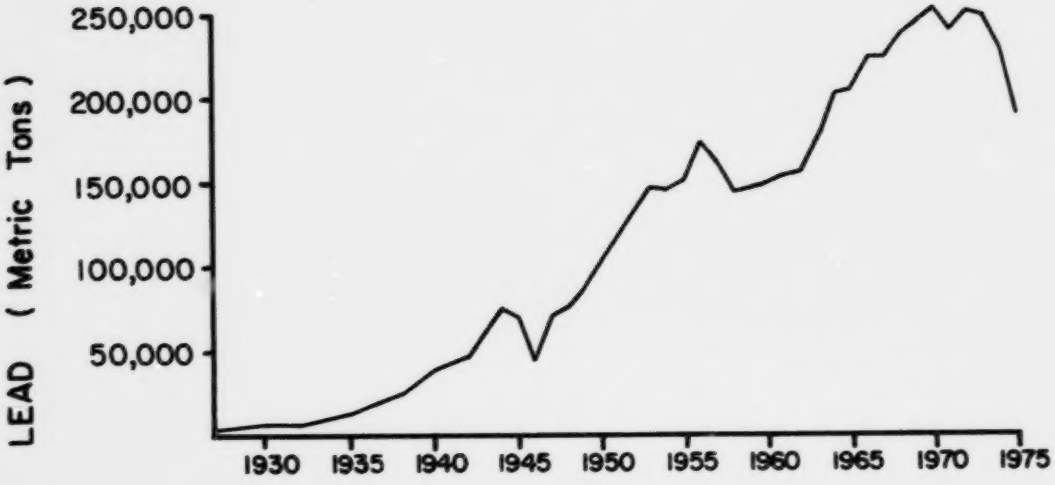

Years B P
0
10
20
30
40
50
100
150
200
250
300
Al and Fe Conc. [mg/g dw]
0
5
10
15
20
25
30
35
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979
Al
Fe

Fig.3-7



Annual consumption of gasoline antiknock additives in the U.S. (from Chow 1978).

Fig.3-8a

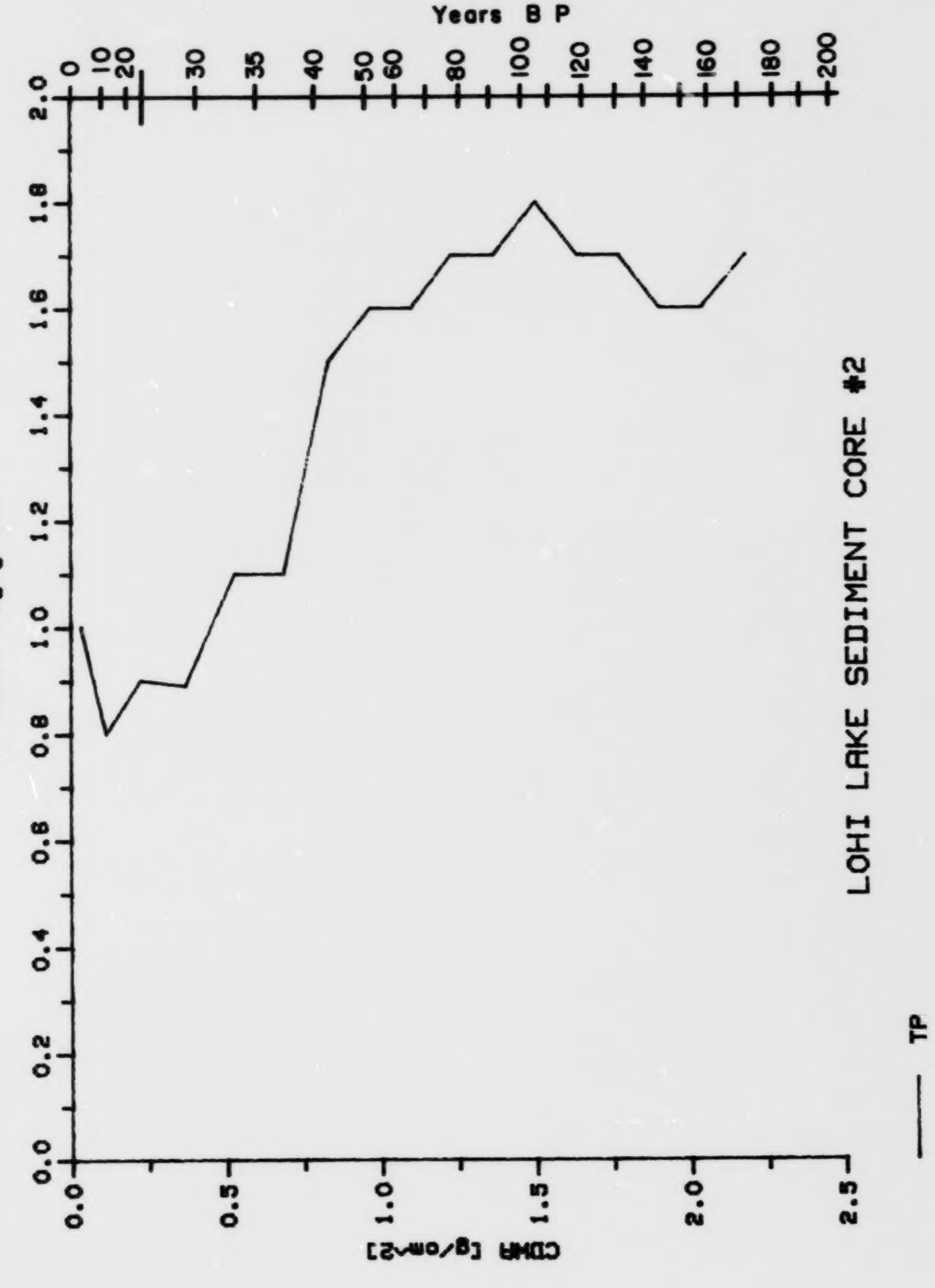

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
TP Conc. [mg/g dw]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2
TP

Fig.3-8b

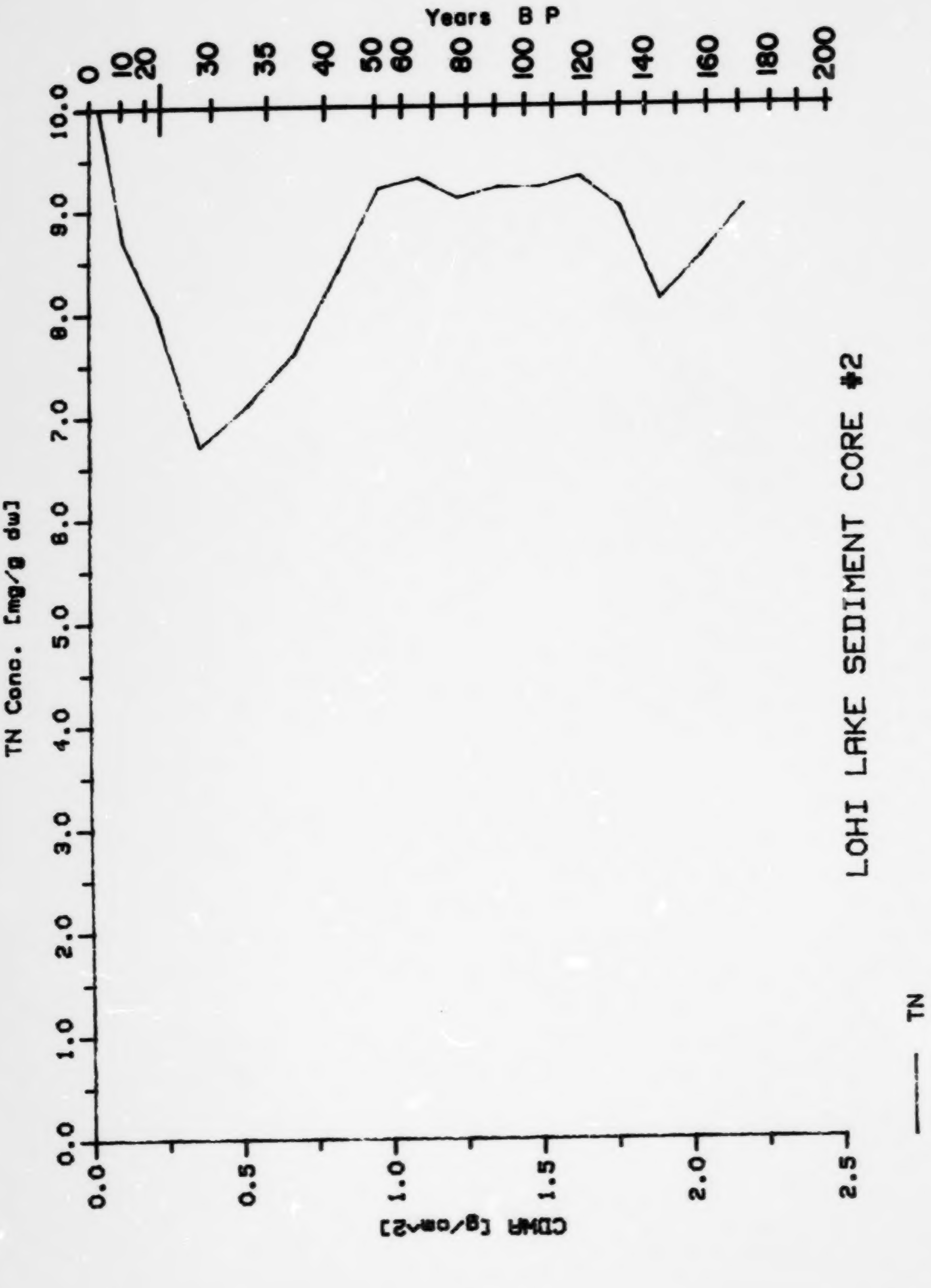

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
TN Conc. [mg/g dw]
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.5
1.0
1.5
2.0
2.5
CDWR [g/cm^2]
LOHI LAKE SEDIMENT CORE #2
TN

Fig.3-9a

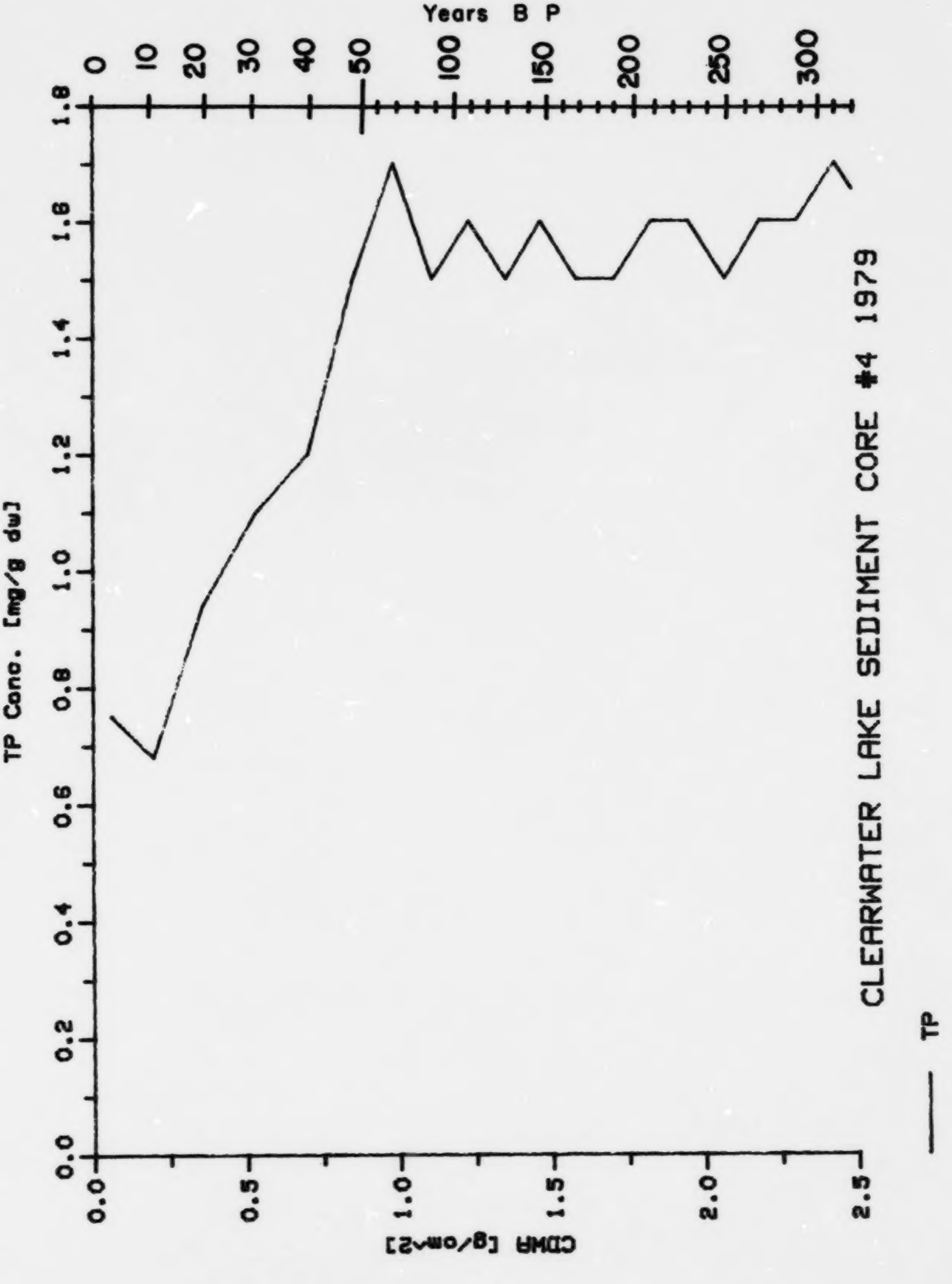

Years B P
0
10
20
30
40
50
100
150
200
250
300
TP Conc. [mg/g dw]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979
TP

Fig.3-9b

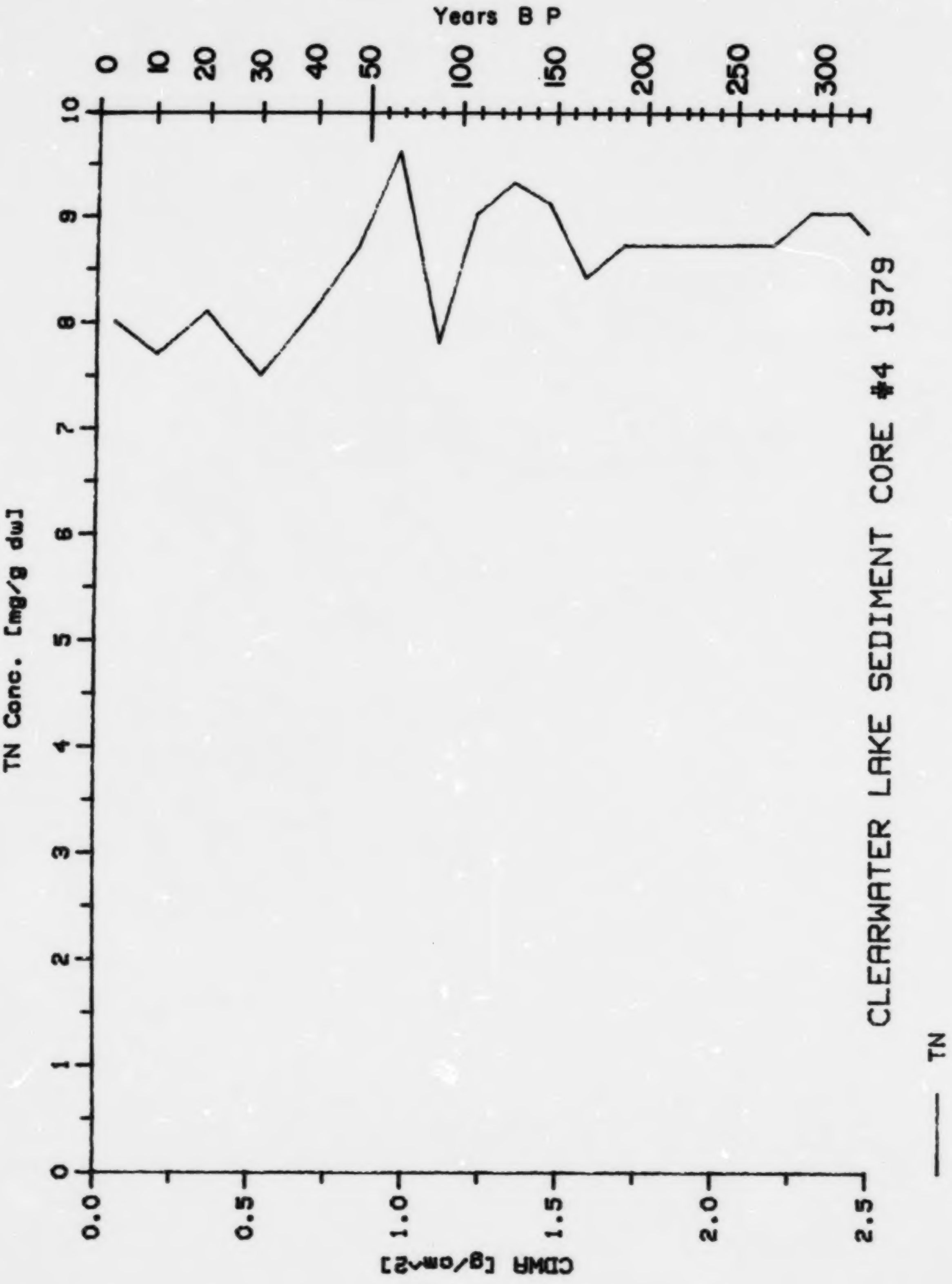

CLEARWATER LAKE SEDIMENT CORE #4 1979
Years B P
0
10
20
30
40
50
100
150
200
250
300
TN Conc. [mg/g dw]
0
1
2
3
4
5
6
7
8
9
10
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
TN

Fig.3-10a

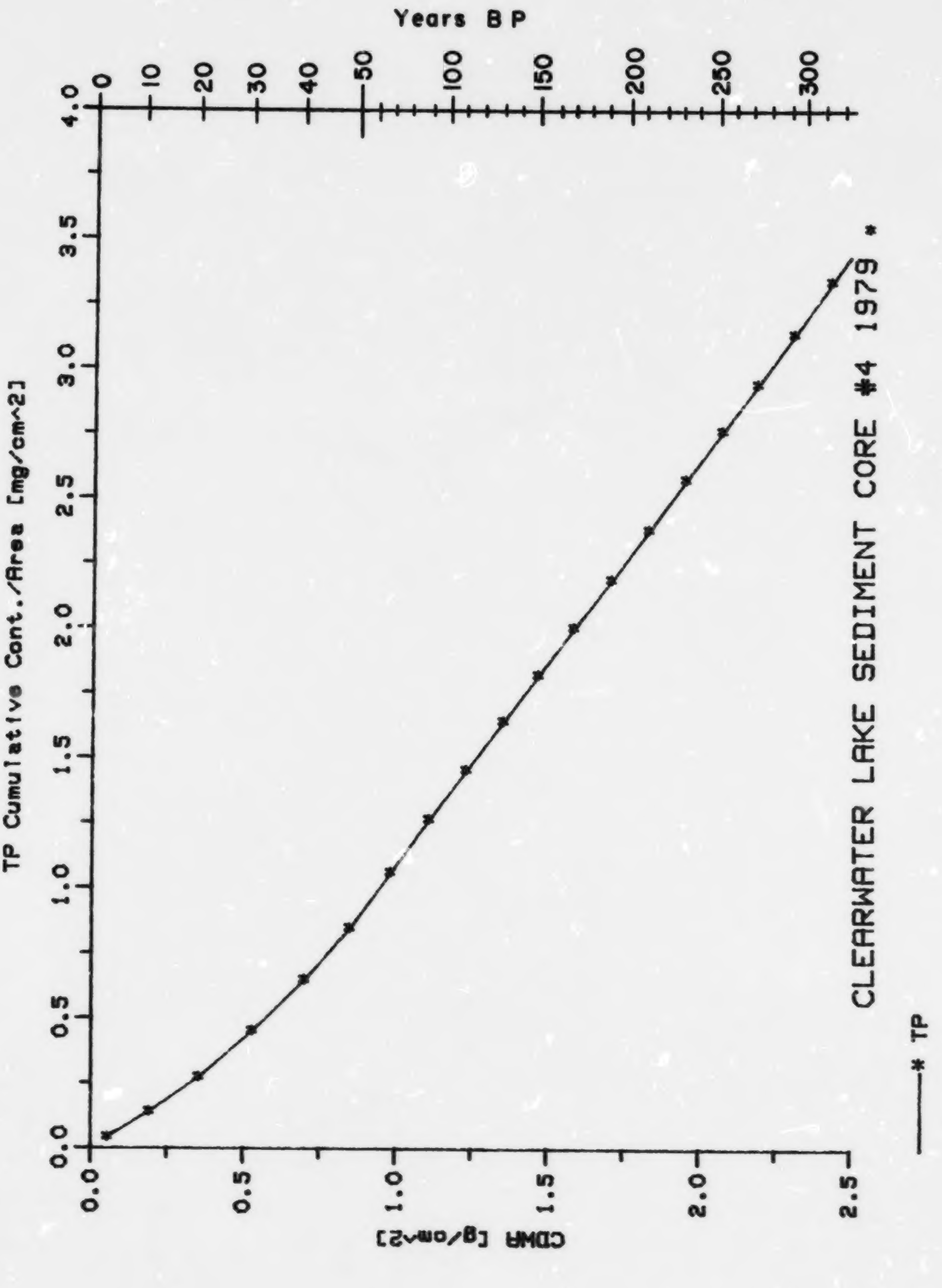

Years BP
0
10
20
30
40
50
100
150
200
250
300
TP Cumulative Cont./Area [mg/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979 *
* TP

Fig.3-10b

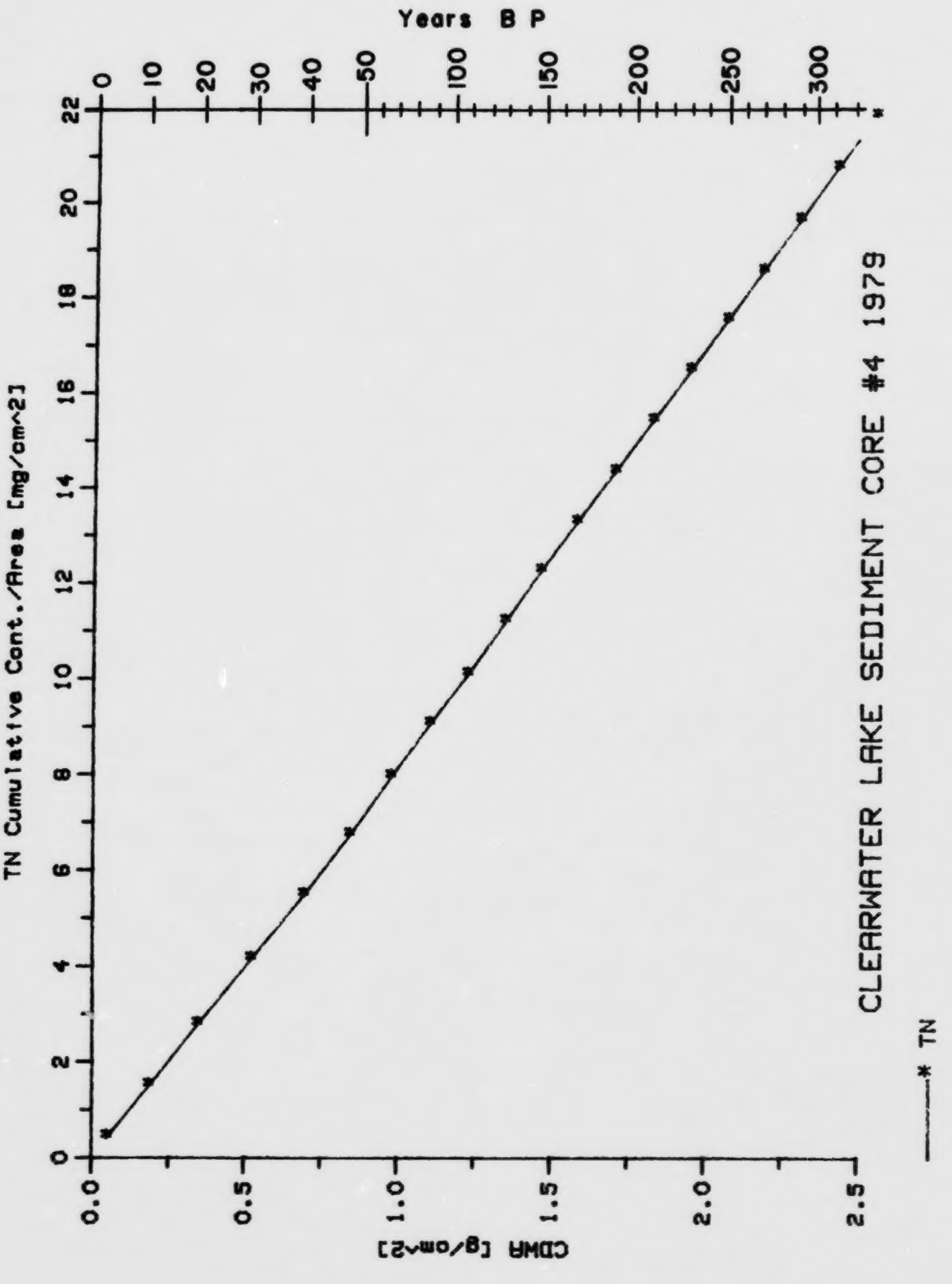

Years B P
0
10
20
30
40
50
100
150
200
250
300
TN Cumulative Cont./Area [mg/cm^2]
0
2
4
6
8
10
12
14
16
18
20
22
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
CLEARWATER LAKE SEDIMENT CORE #4 1979
* TN

Fig.3-11a

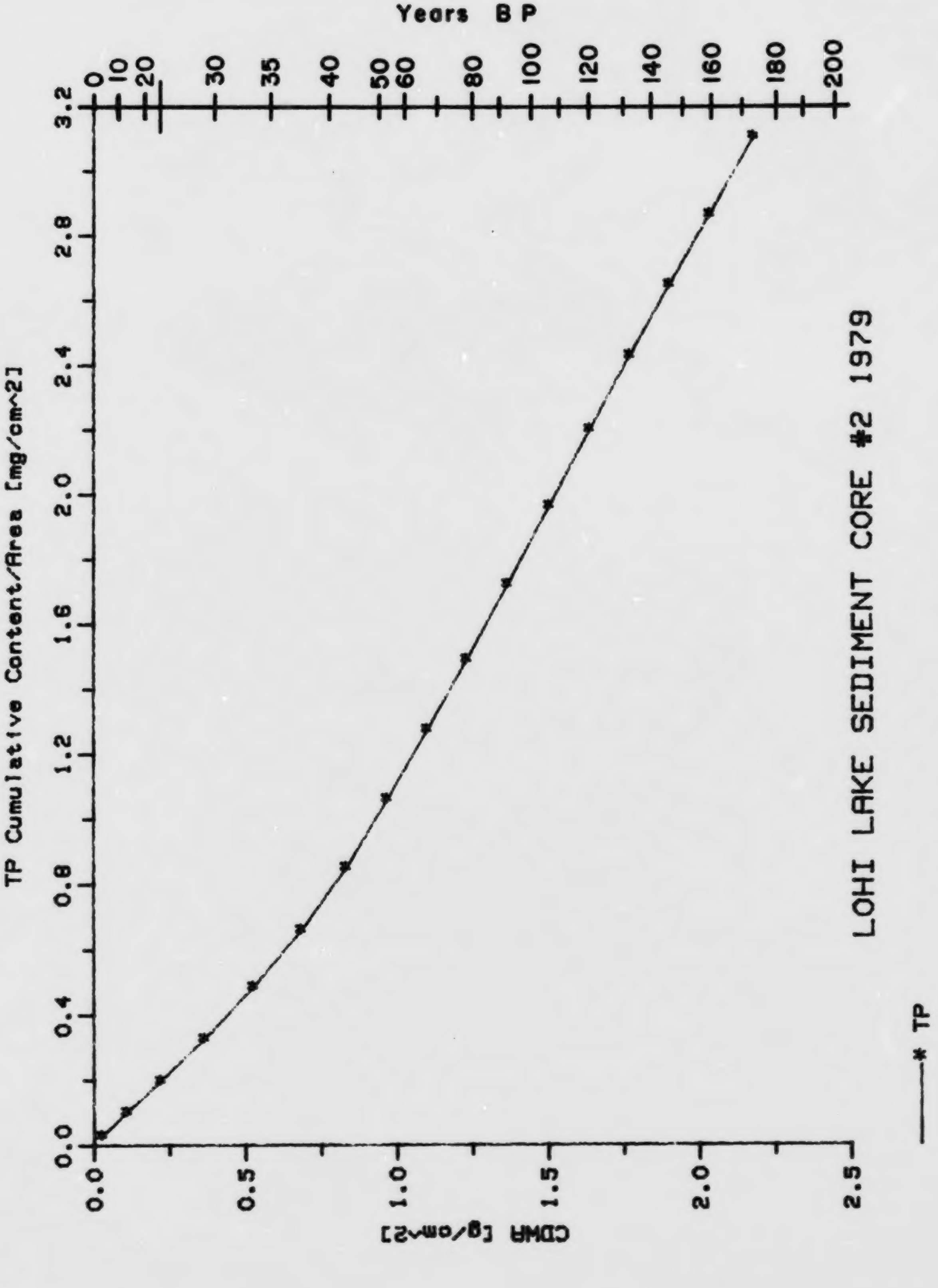

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
TP Cumulative Content/Area [mg/cm^2]
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2 1979
* TP

Fig.3-11b

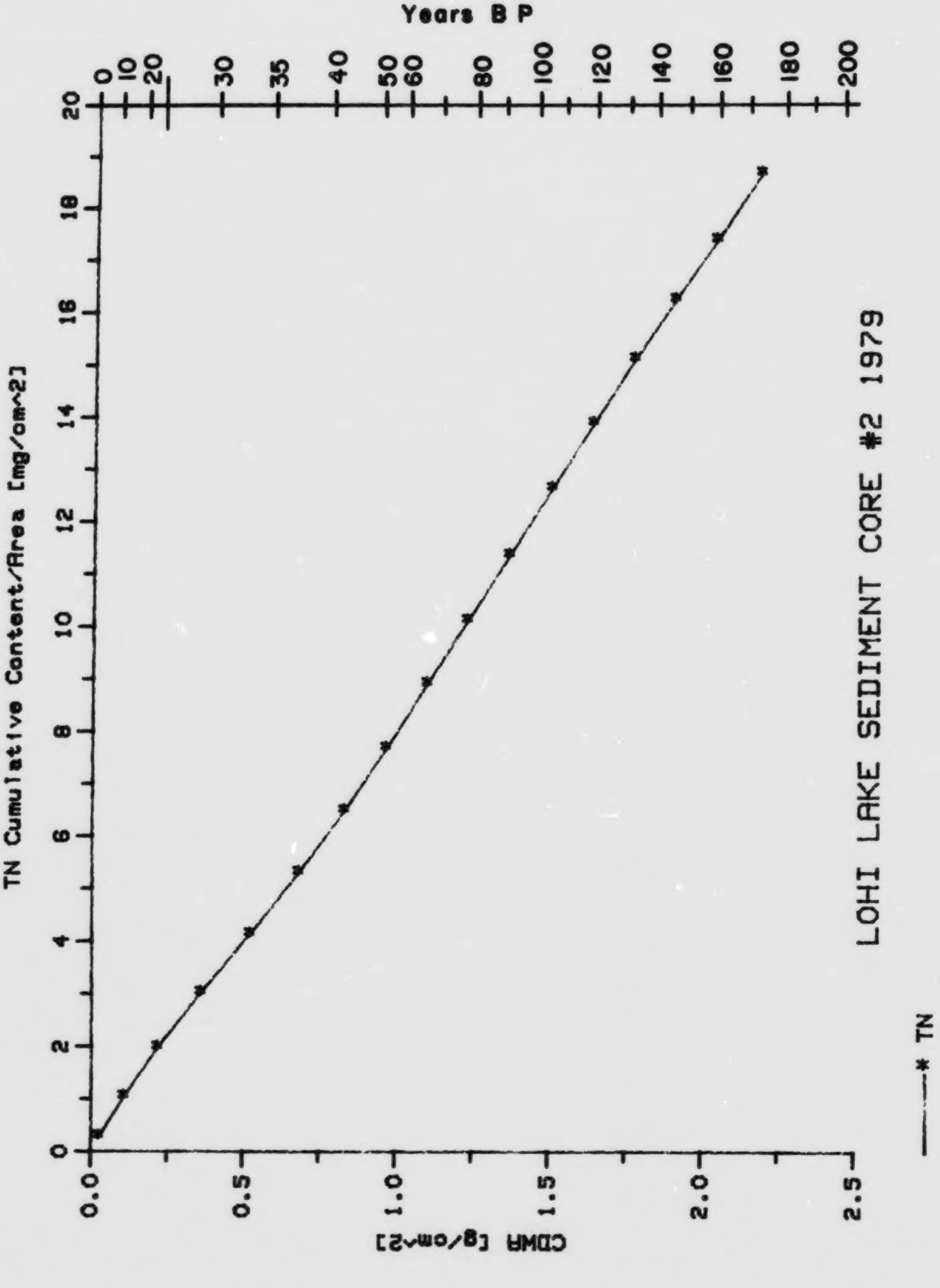

Years B P
0
10
20
30
35
40
50
60
80
100
120
140
160
180
200
TN Cumulative Content/Area [mg/cm^2]
0
2
4
6
8
10
12
14
16
18
20
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
LOHI LAKE SEDIMENT CORE #2 1979
* TN

Fig.3-12

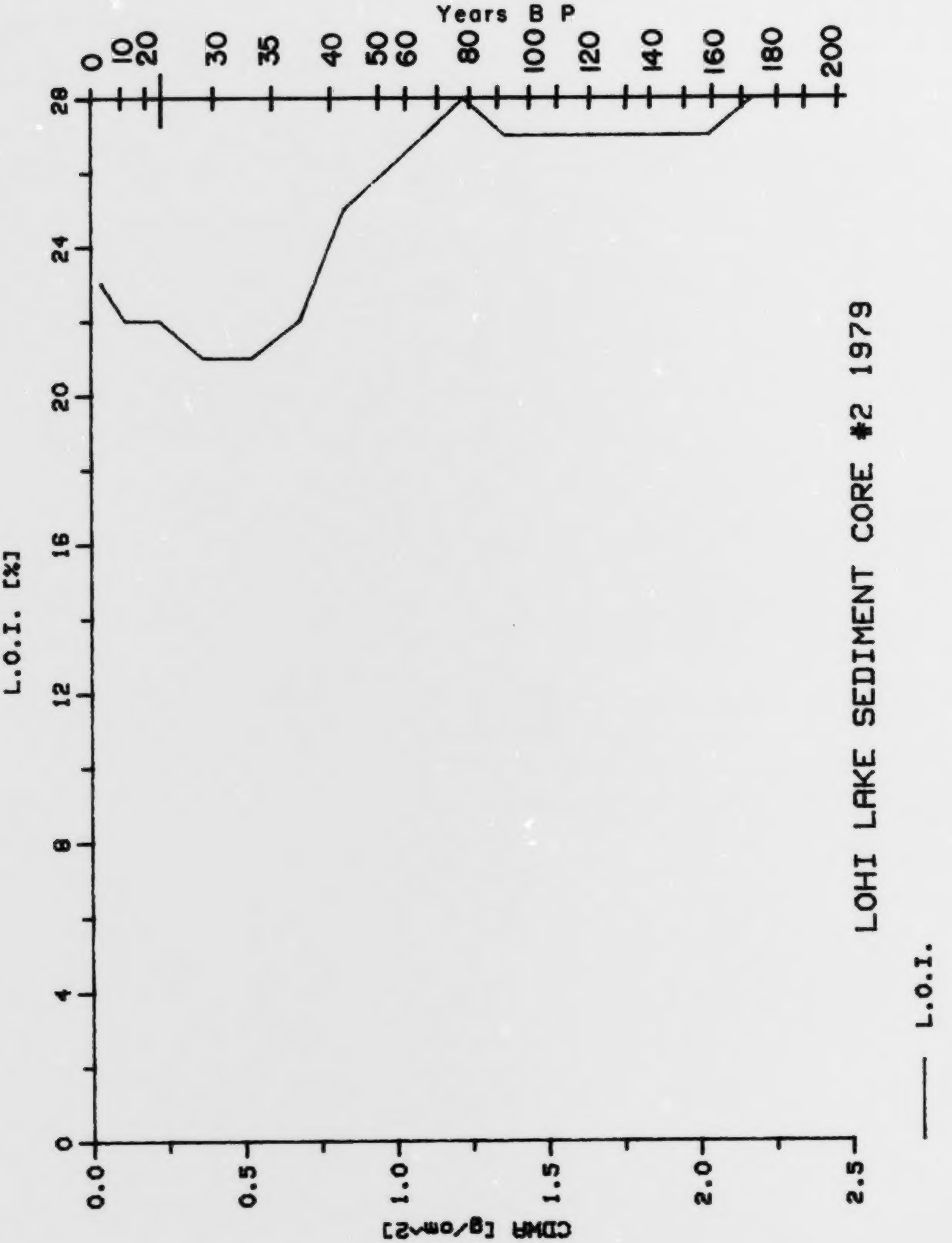

LOHI LAKE SEDIMENT CORE #2 1979

Fig.3-13

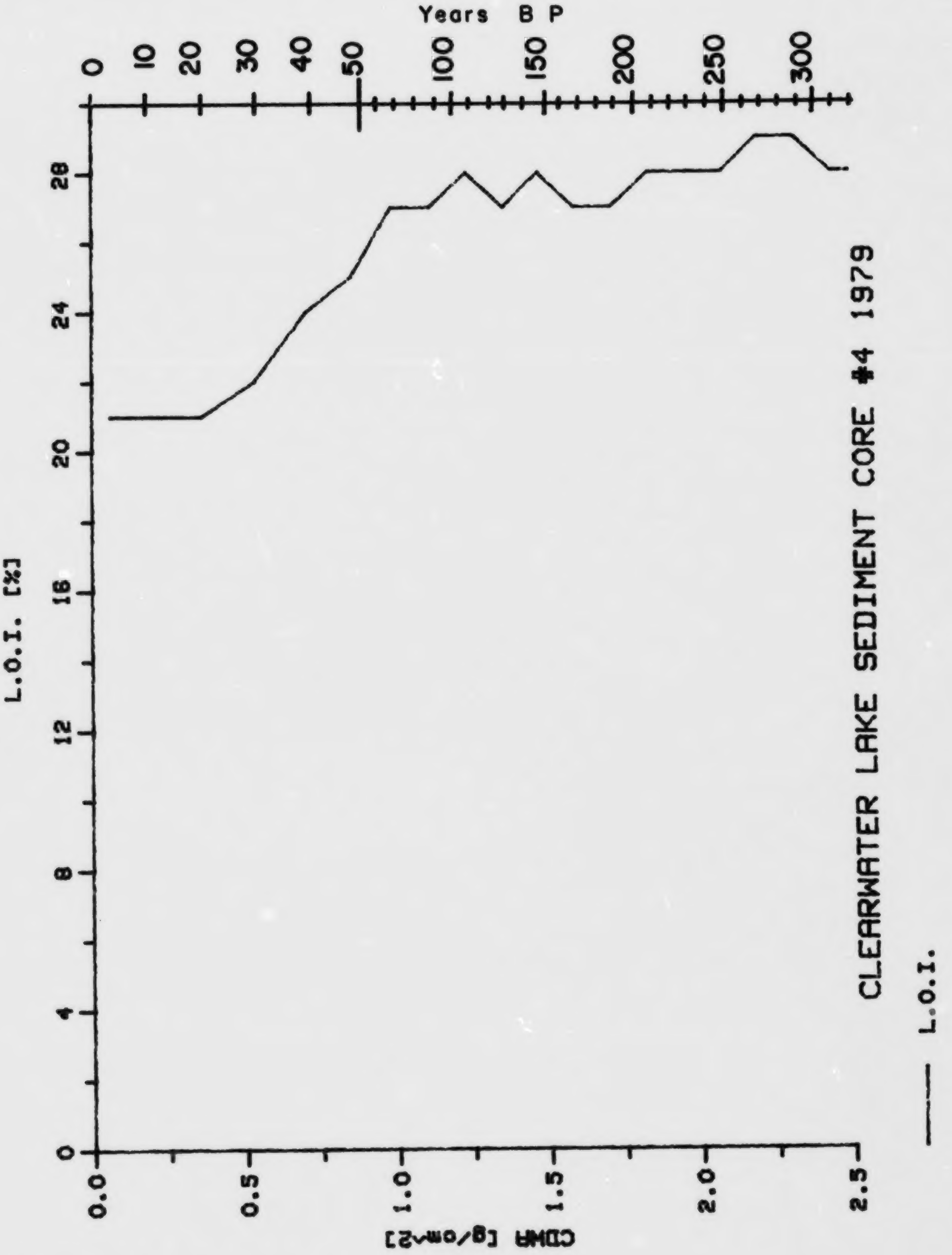

Years B P
0
10
20
30
40
50
100
150
200
250
300
L.O.I. [%]
0
4
8
12
16
20
24
28
0.0
0.5
1.0
1.5
2.0
2.5
CDWR [g/cm^2]
CLEARWATER LAKE SEDIMENT CORE #4 1979
— L.O.I.

Fig.3-14

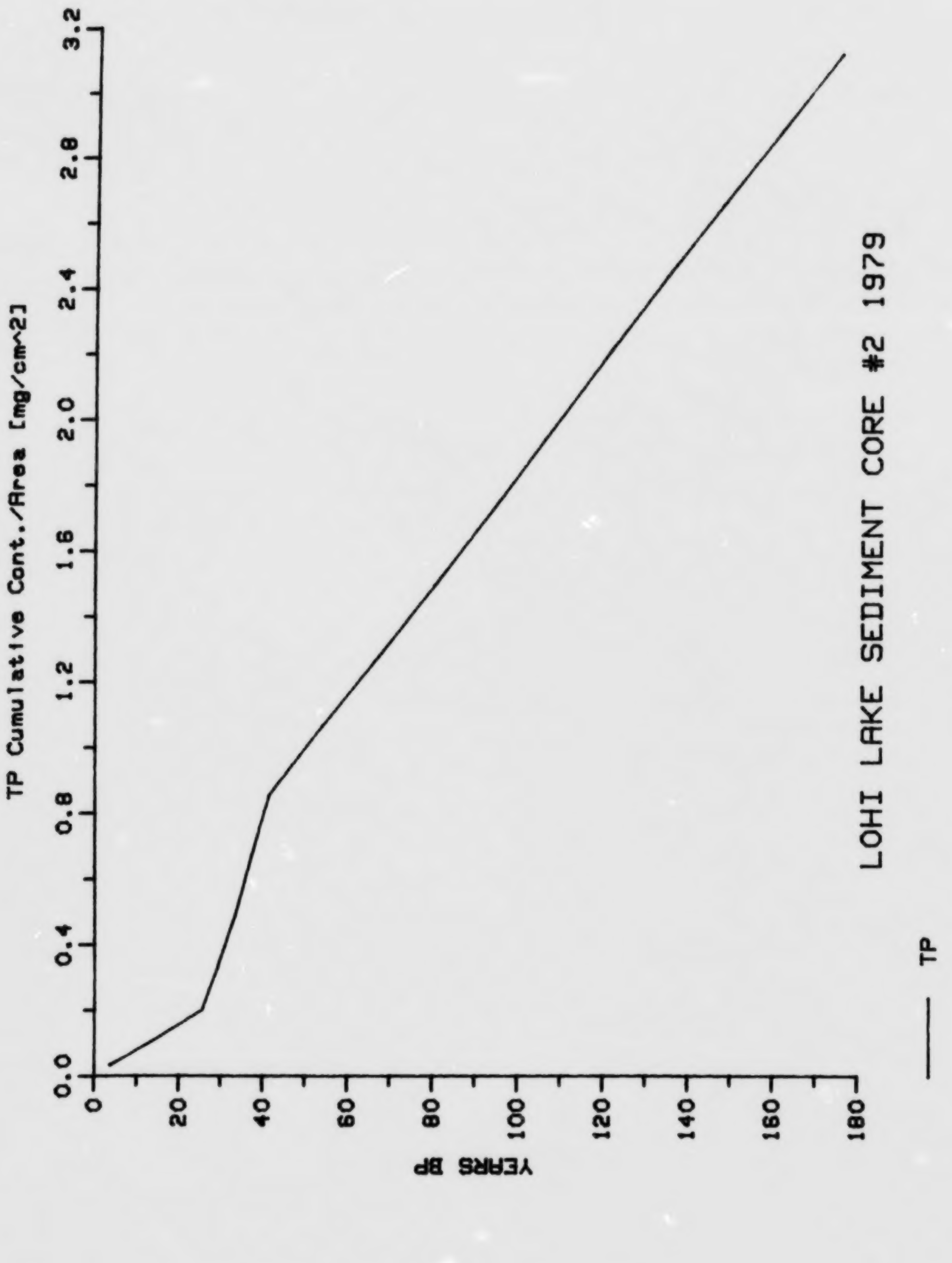
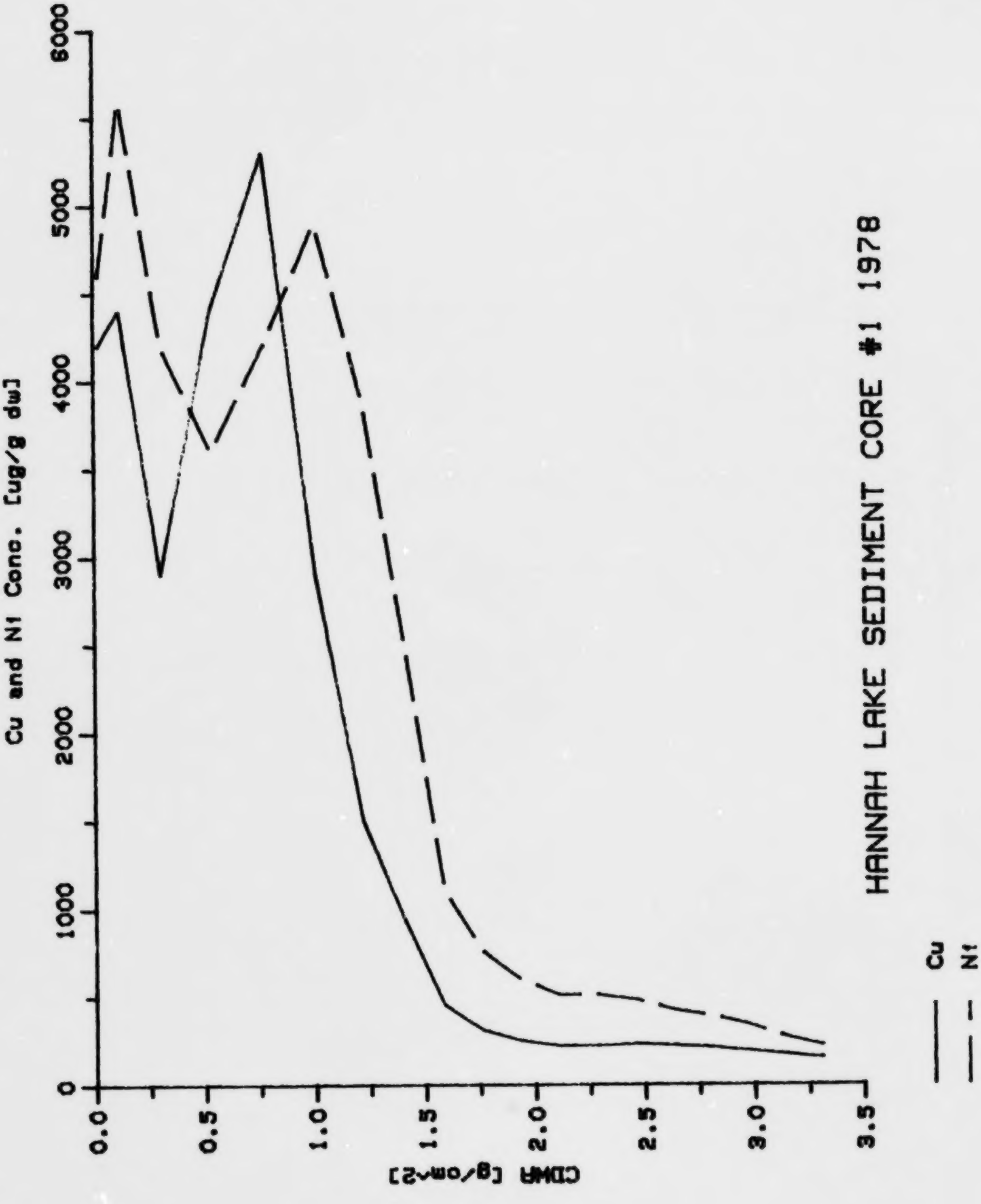

LOHI LAKE SEDIMENT CORE #2 1979
TP Cumulative Cont./Area [mg/cm^2]
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
YEARS BP
0
20
40
60
80
100
120
140
160
180
TP

Fig.3-15a



HANNAH LAKE SEDIMENT CORE #1 1978

Fig.3-15b

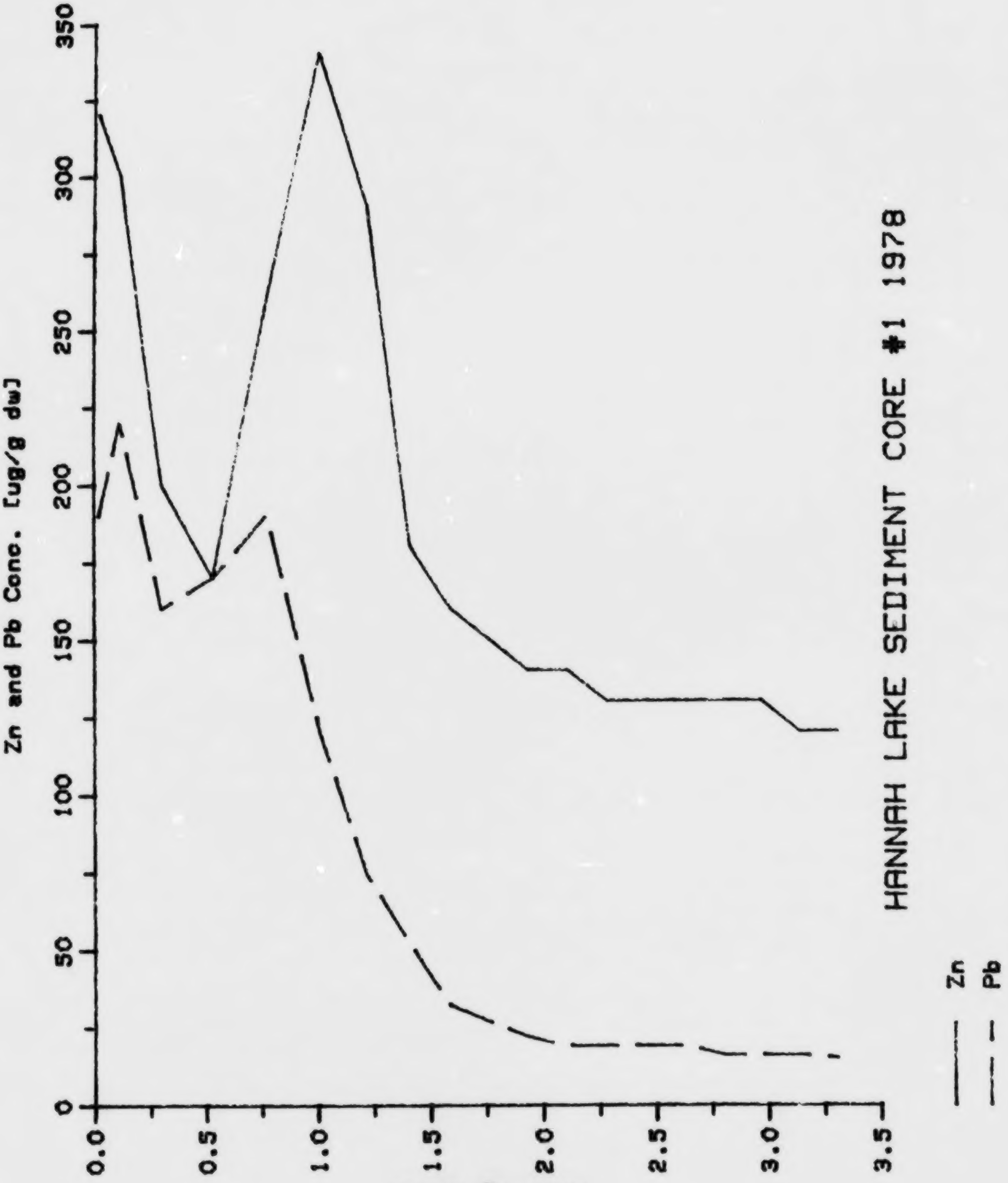

HANNAH LAKE SEDIMENT CORE #1 1978
Zn and Pb Conc. [ug/g dw]
CDWA [g/cm^2]
0
50
100
150
200
250
300
350
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Zn
Pb

Fig.3-15c

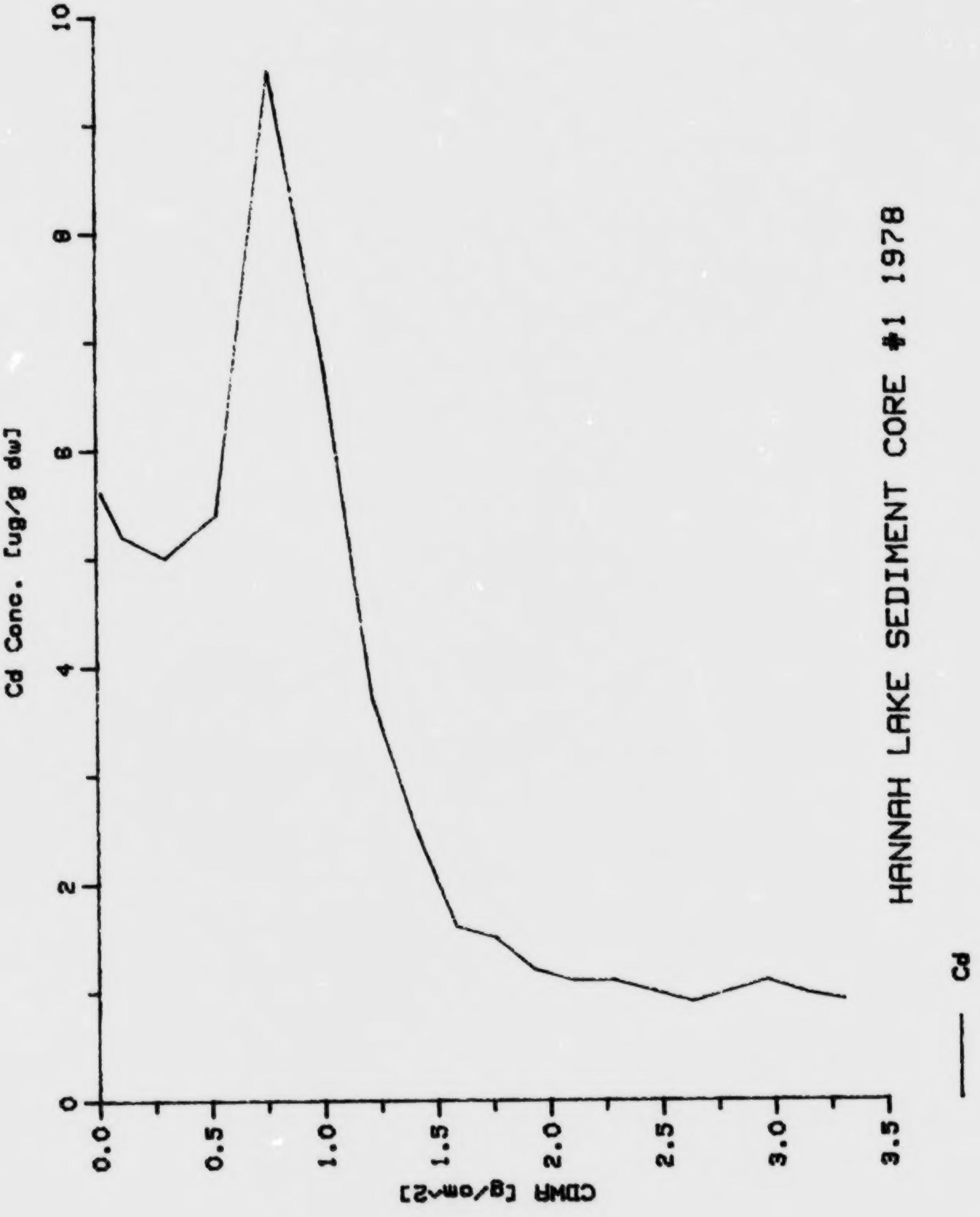

HANNAH LAKE SEDIMENT CORE #1 1978
Cd Conc. [ug/g dw]
CDWR [g/cm^2]
0
2
4
6
8
10
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Cd

Fig.3-15d

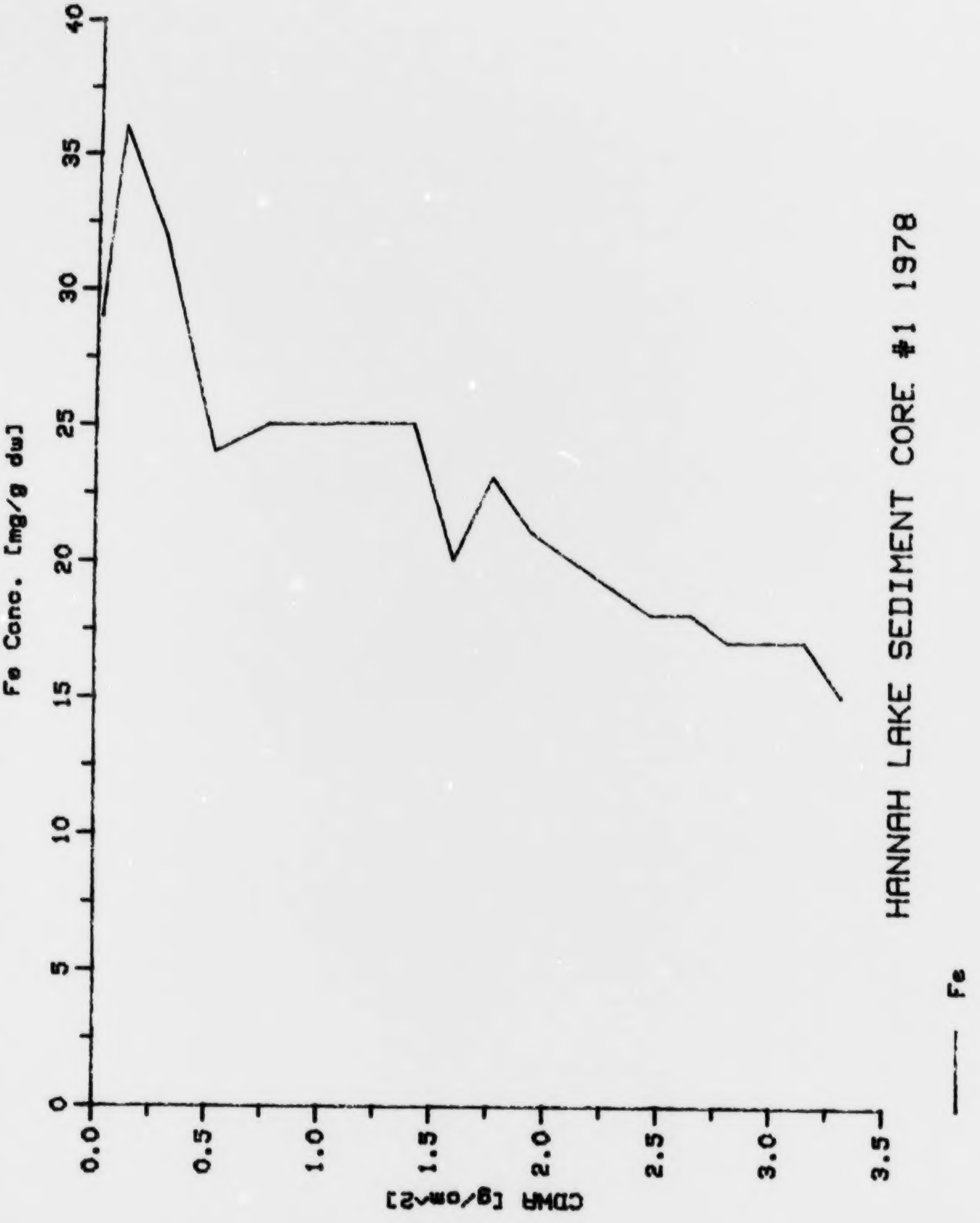

HANNAH LAKE SEDIMENT CORE #1 1978
Fe Conc. [mg/g dw]
CDWA [g/cm^2]
Fe
0
5
10
15
20
25
30
35
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

Fig.3-16a

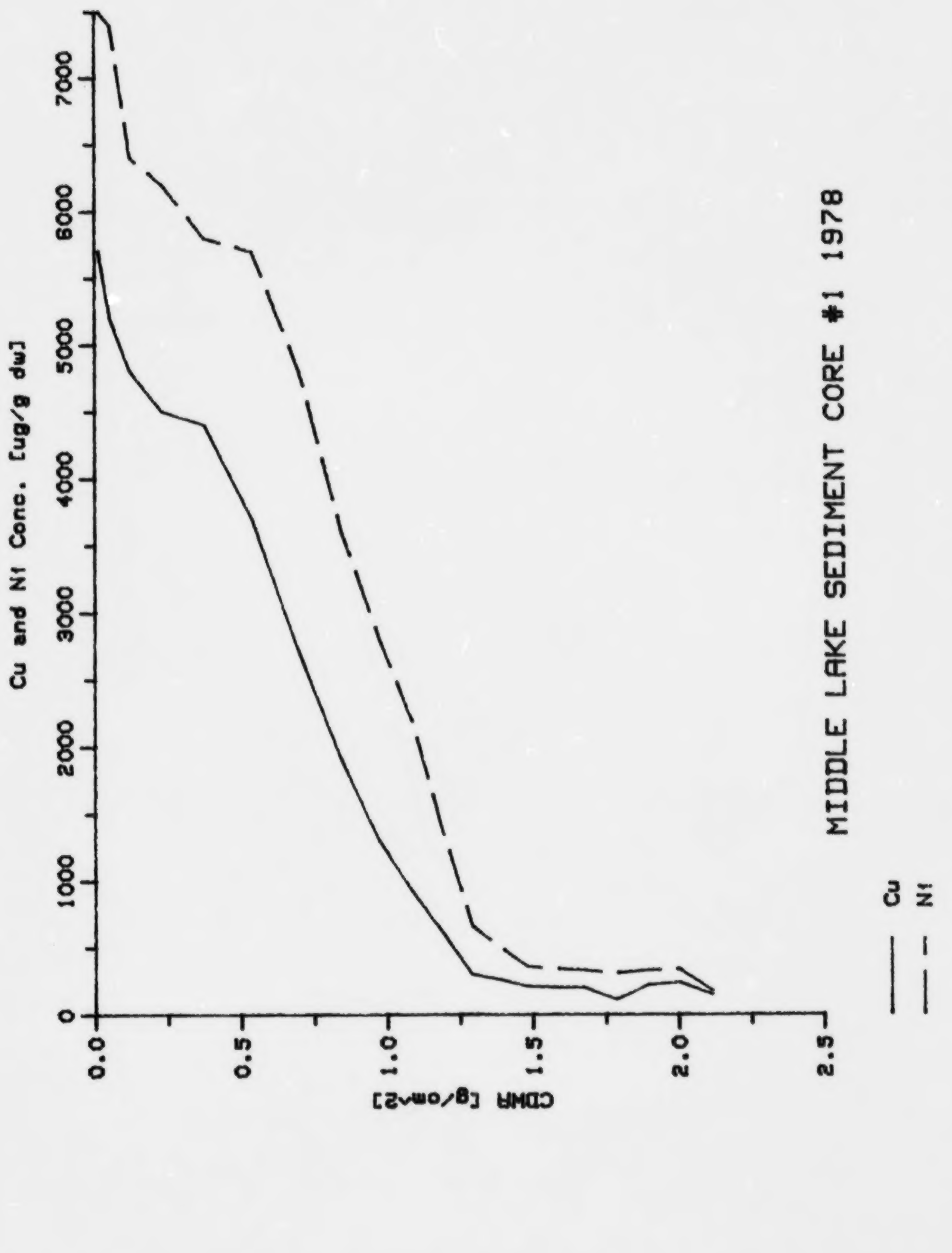

MIDDLE LAKE SEDIMENT CORE #1 1978
Cu and Ni Conc. [ug/g dw]
0
1000
2000
3000
4000
5000
6000
7000
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
Cu
Ni

Fig.3-16b

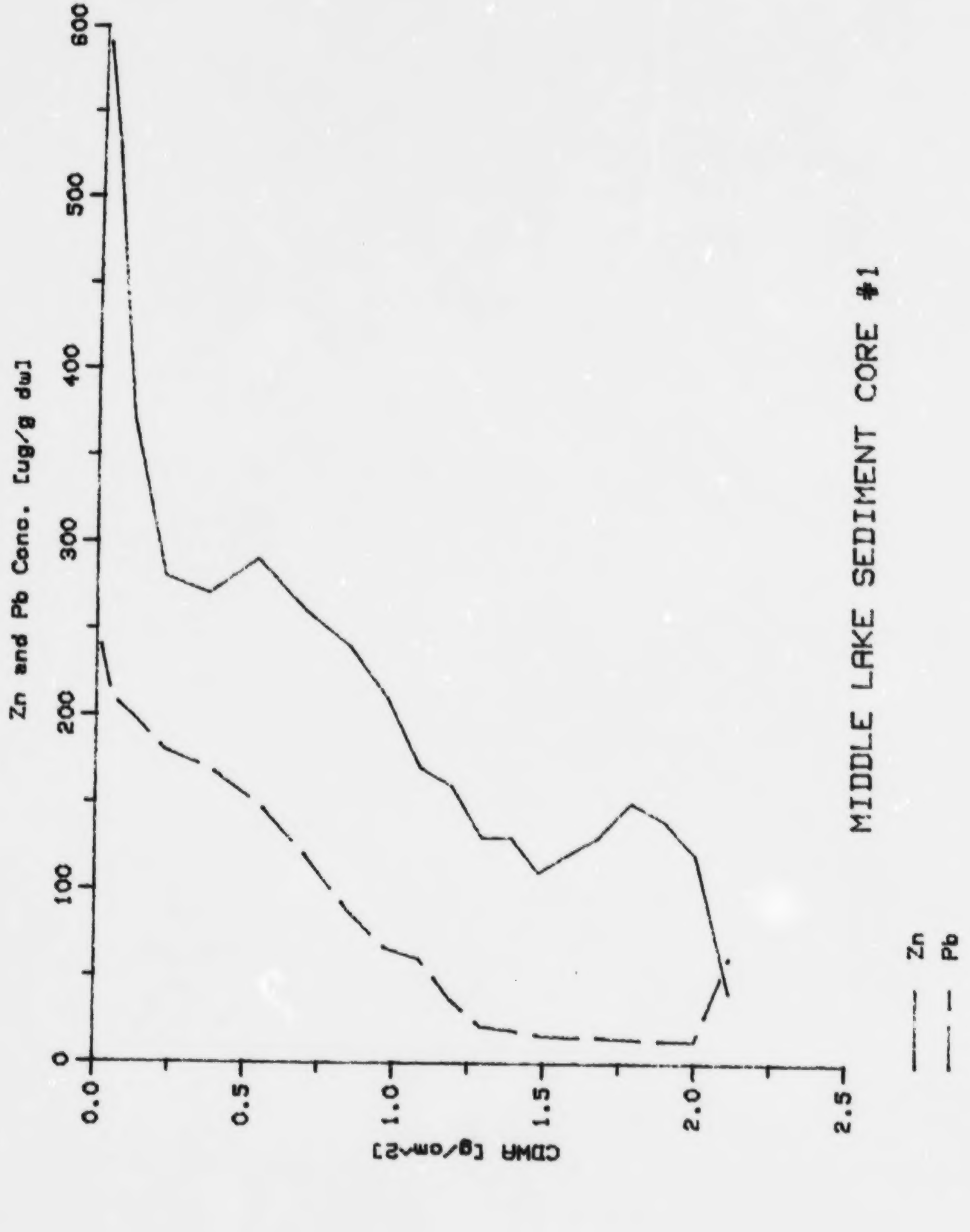

MIDDLE LAKE SEDIMENT CORE #1
Zn and Pb Conc. [ug/g dw]
0
100
200
300
400
500
600
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
Zn
Pb

Fig.3-16c

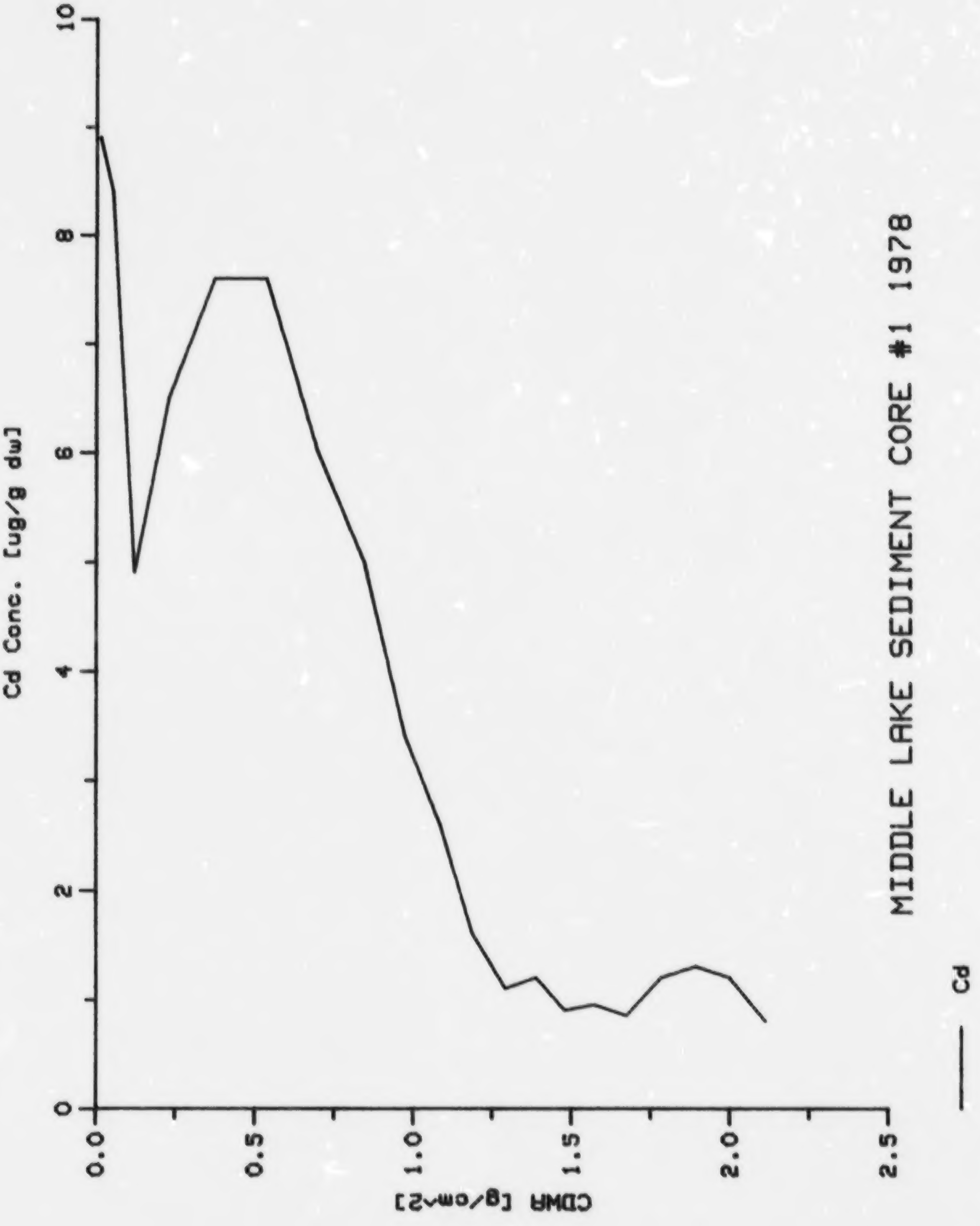

MIDDLE LAKE SEDIMENT CORE #1 1978
Cd Conc. [ug/g dw]
0
2
4
6
8
10
0.0
0.5
1.0
1.5
2.0
2.5
CDWR [g/cm^2]
Cd

Fig.3-16d

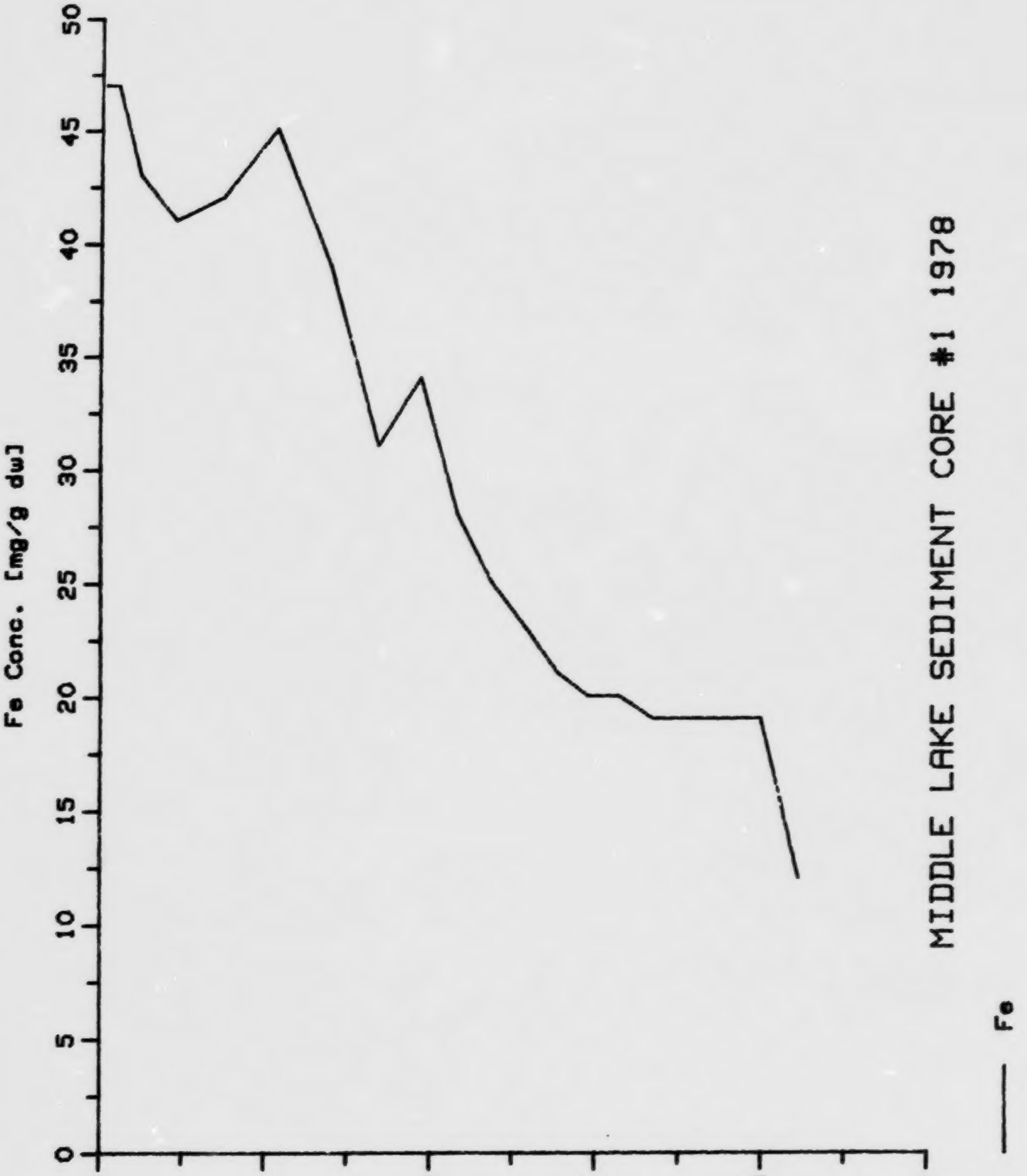

MIDDLE LAKE SEDIMENT CORE #1 1978

Fig.3-17a

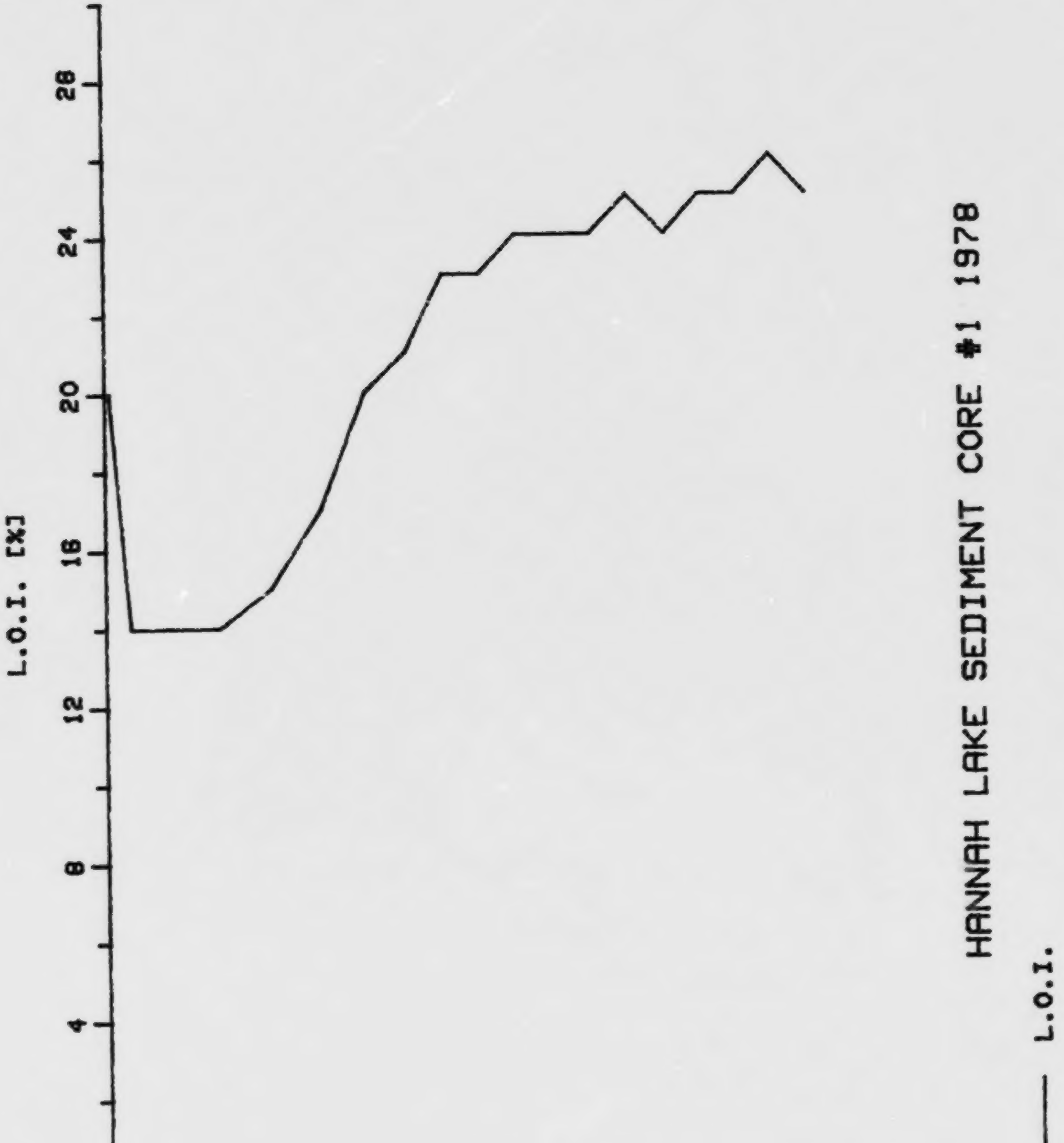
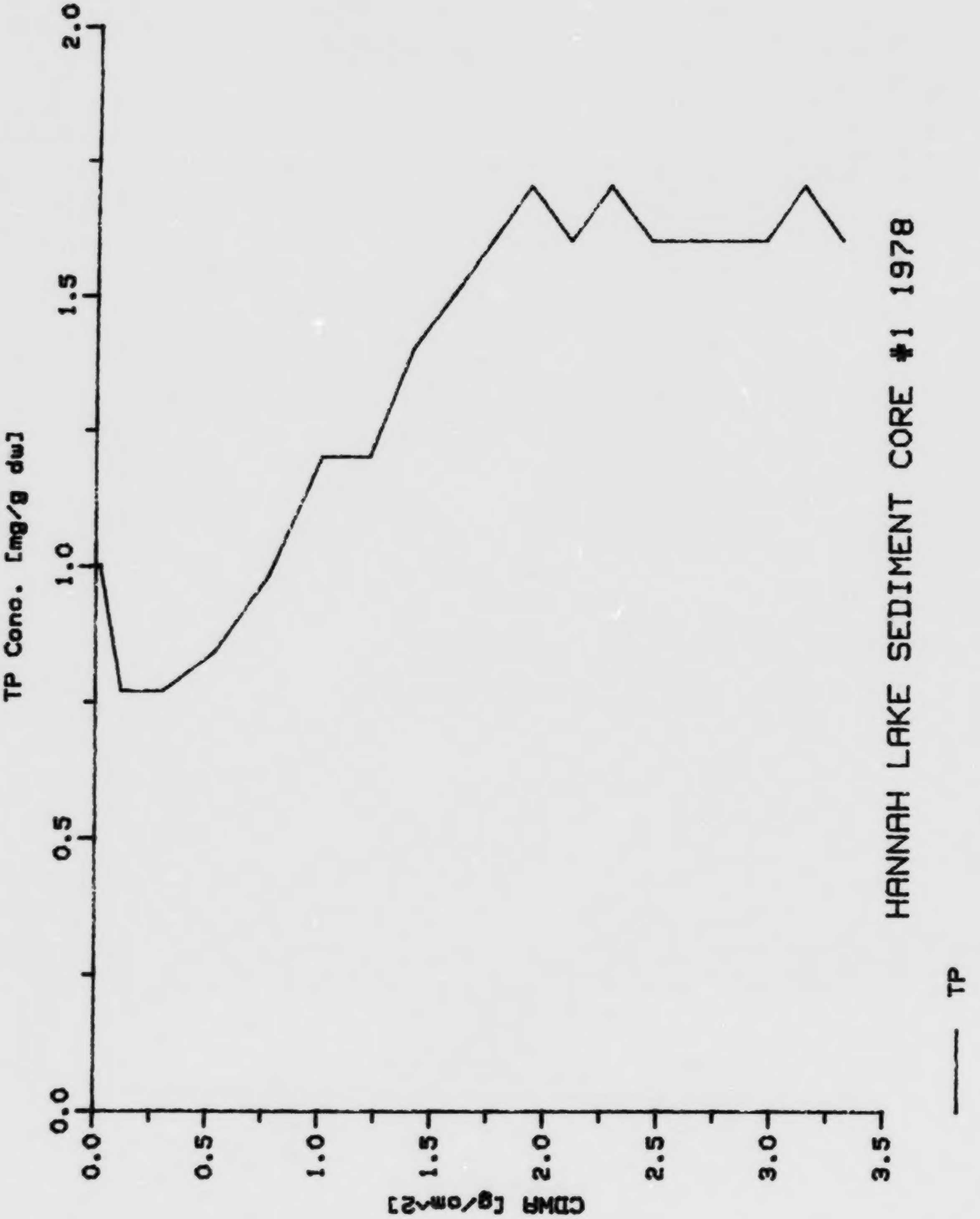

HANNAH LAKE SEDIMENT CORE #1 1978
L.O.I. [%]
0
4
8
12
16
20
24
28
0.0
1.0
2.0
3.0
4.0
CDWR [g/cm^2]
L.O.I.

Fig.3-17b



HANNAH LAKE SEDIMENT CORE #1 1978
TP Conc. [mg/g dw]
0.0
0.5
1.0
1.5
2.0
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
TP

Fig.3-17c

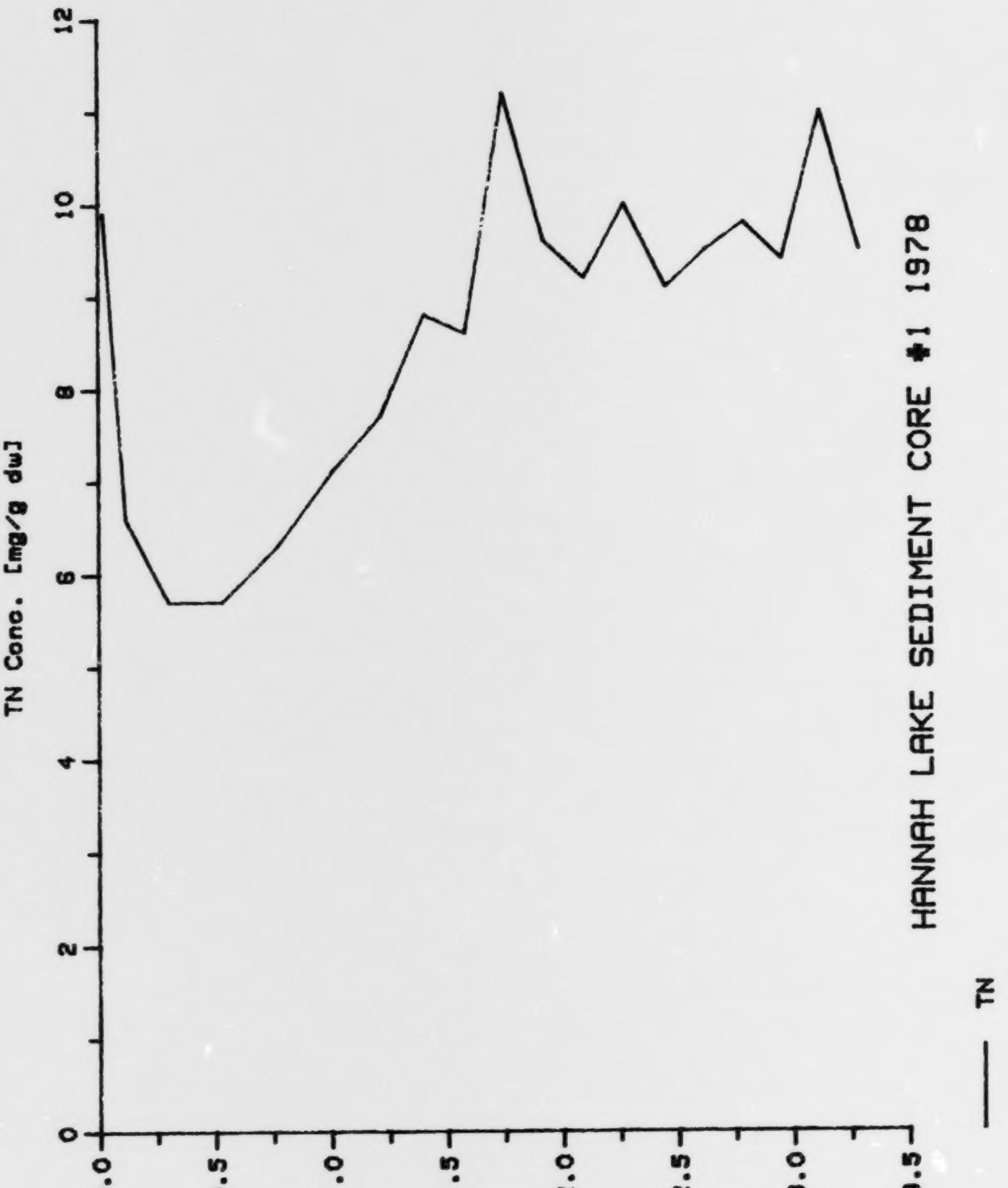

HANNAH LAKE SEDIMENT CORE #1 1978
TN Conc. [mg/g dw]
0
2
4
6
8
10
12
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
TN

Fig.3-18a

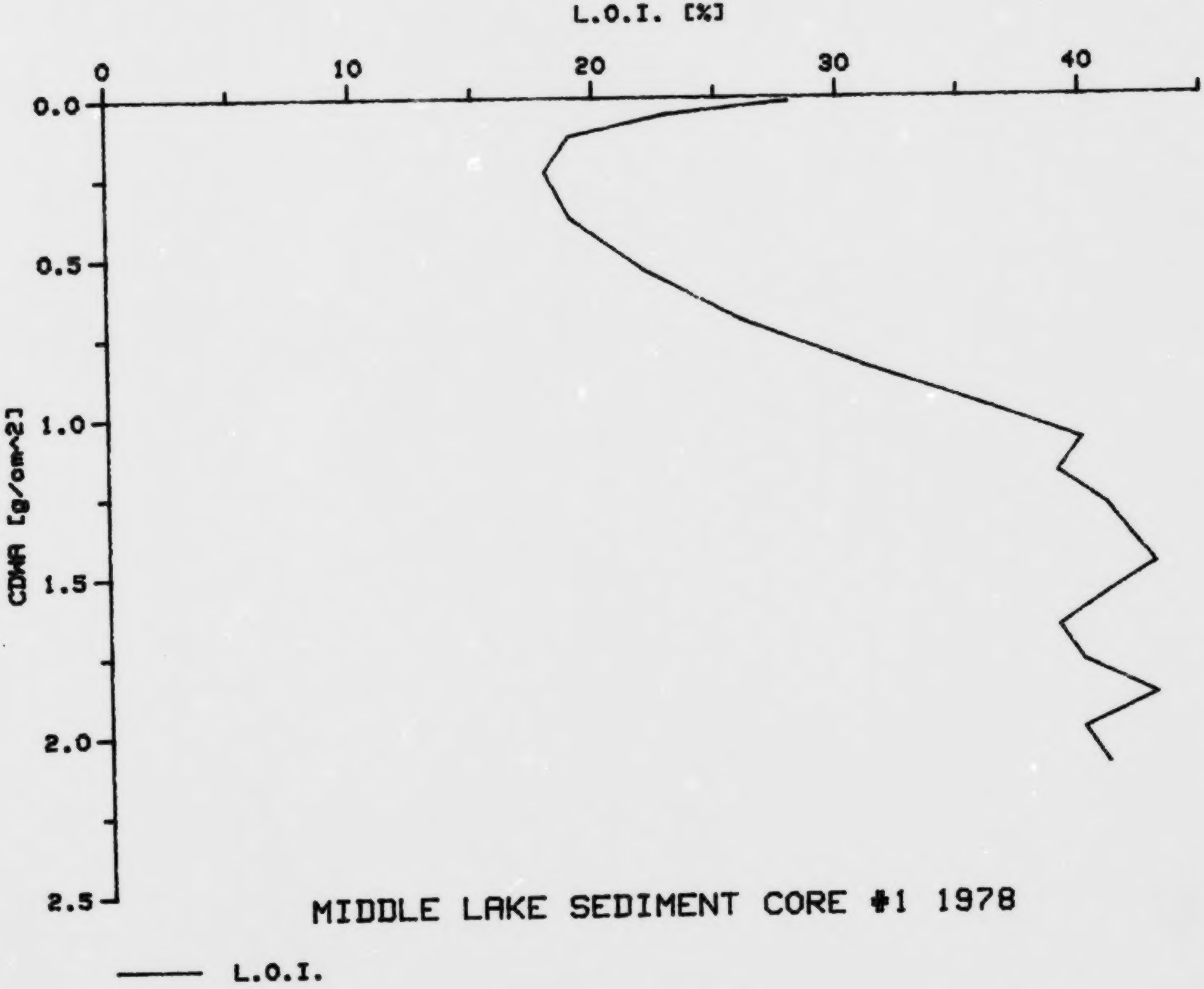
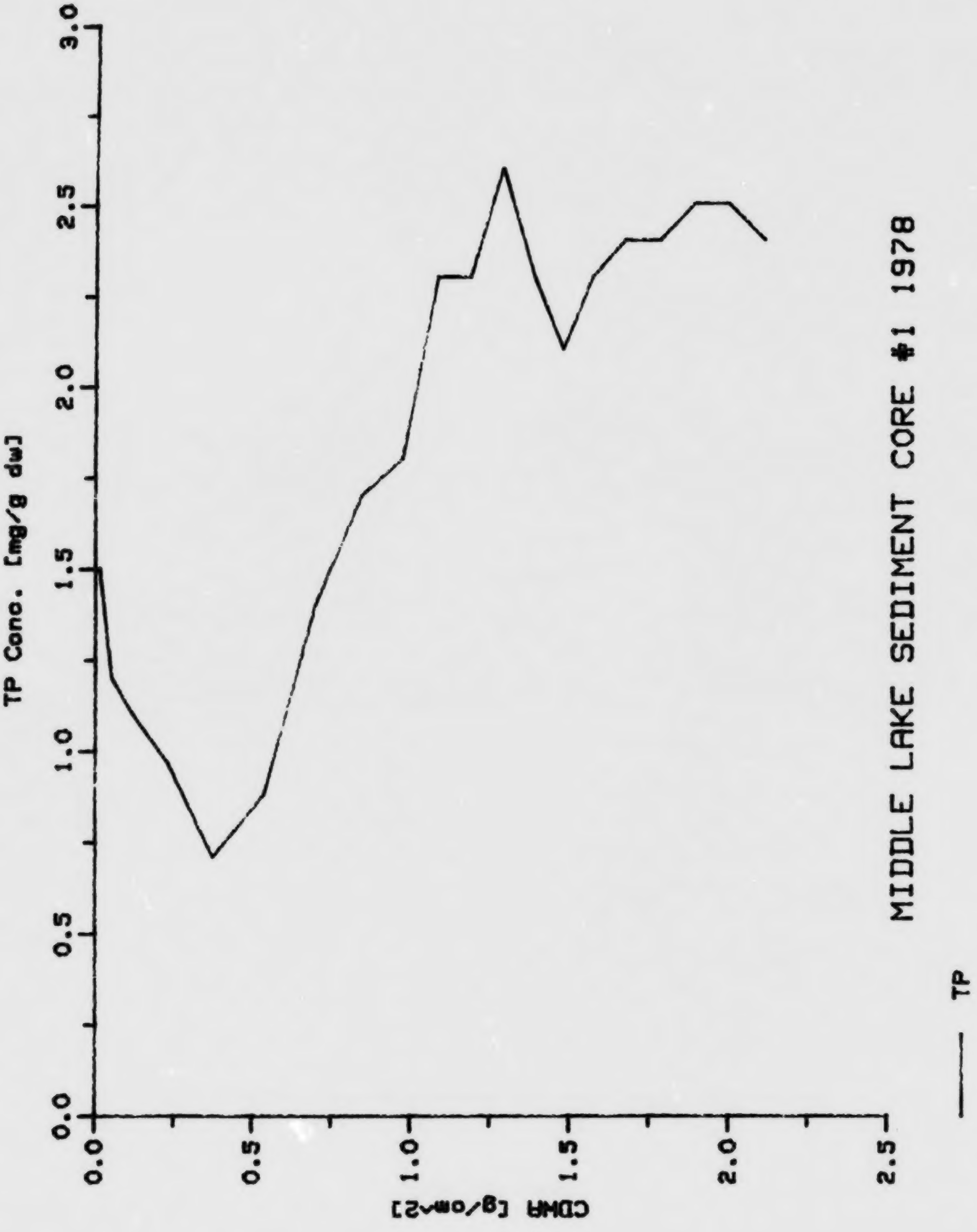
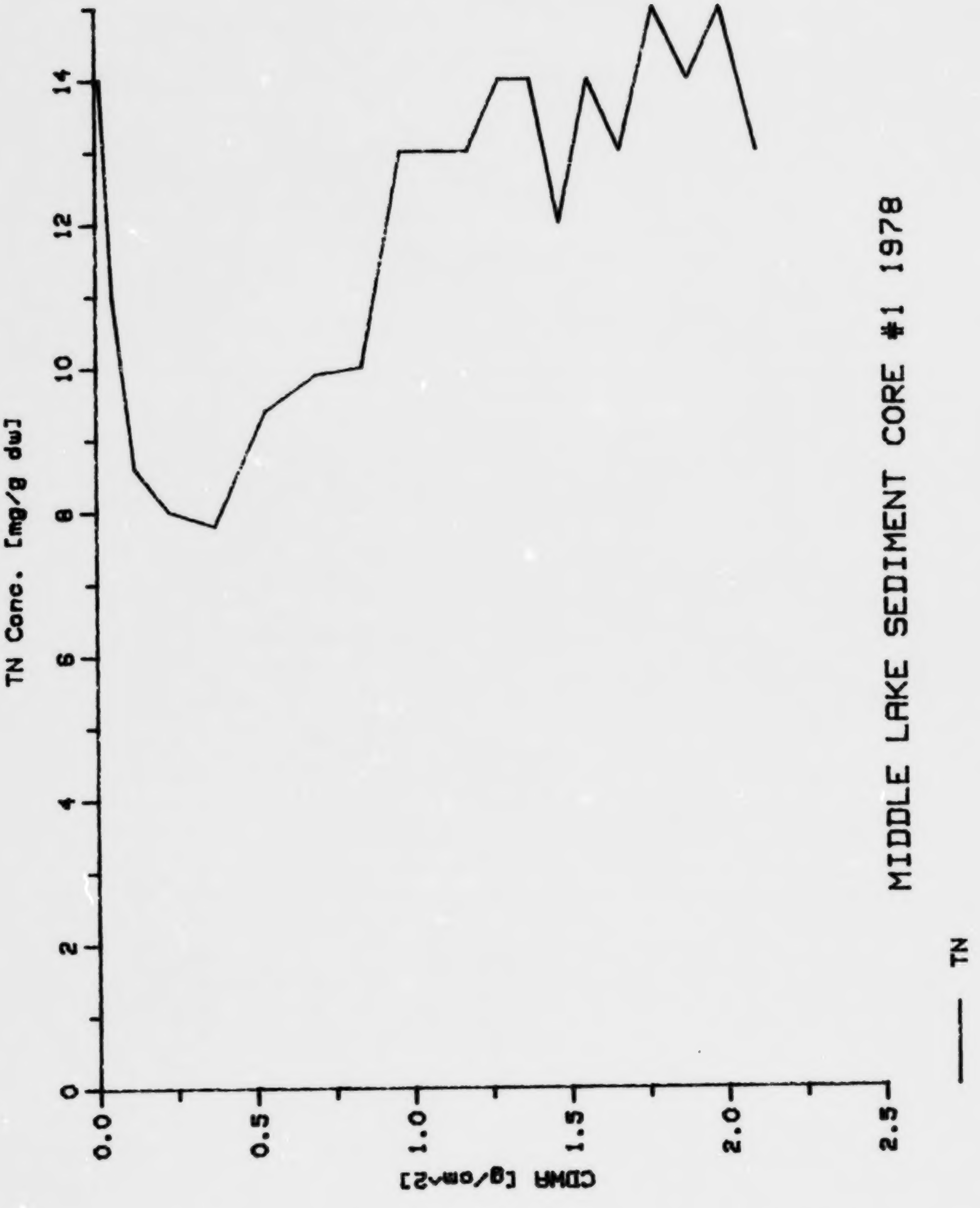

L.O.I. [%]
0
10
20
30
40
CDWA [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
MIDDLE LAKE SEDIMENT CORE #1 1978
L.O.I.

Fig.3-18b



MIDDLE LAKE SEDIMENT CORE #1 1978

Fig.3-18c


MIDDLE LAKE SEDIMENT CORE #1 1978
TN Conc. [mg/g dw]
0
2
4
6
8
10
12
14
CDWR [g/cm^2]
0.0
0.5
1.0
1.5
2.0
2.5
TN

CHAPTER 4

COMPONENTS OF THE WATER BALANCE OF LAKES NEAR SUDBURY, ONTARIO

W.A. Scheider

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A. Introduction

The flux of chemicals in lakes and watersheds is intimately tied to the hydrological cycle because water acts as a solvent and transporting agent. Hydrological data are therefore a necessity for evaluation of chemical mass balances. A useful means of presenting hydrological data is in the form of a water balance. For a lake, the water balance may be described by the following equation:

$$P + R - E - O \pm G = S \tag{4-1}$$

where: P = precipitation to the lake surface

R = surface runoff into the lake

E = evaporation from the lake

O = outflow from the lake

G = net ground water gain or loss by the lake

S = change in lake storage

In the preceding definitions, surface runoff includes channelized drainage from the terrestrial portion of the lake's watershed that is measured at a hydrological gauging station, channelized drainage that is not gauged and non-channelized drainage or direct runoff (Newbury and Beaty 1977). The groundwater term includes the direct gain or loss of groundwater from lakes, not that fraction of the surface runoff that has a groundwater origin.

The basis for the water balance equation is the principle of conservation of mass and the units are mass per interval of time. Assuming a constant density for water, the units become volume per interval of time. As in any water balance, not all components of the equation can be directly measured but must rather be estimated. Those components that can be measured include precipitation, runoff from gauged areas of the terrestrial basin (channelized drainage that is gauged), outflow from the lake and change in lake storage. The elusive components of the balance are evaporation, runoff from ungauged areas of the terrestrial basin (channelized drainage that is not gauged and direct runoff) and groundwater.

A strength of the water balance approach is that it can be used to test the various components if each is measured or estimated separately and none obtained as a residual. If a reasonable (within 10%) balance is not achieved, all components should be re-evaluated. However, a fortuitous balance may occur as the result of compensating errors.

In this chapter, data for each component of the water balance of Hannah, Middle, Clearwater, Lohi and Nelson Lakes are presented from June 1977 to December 1979. Variability in components between lakes and/or watersheds is discussed. A water balance for the 1978 and 1979 calender years only is presented because these annual periods have the most complete hydrological data.

B. Description of Study Area

The locations of the 5 study lakes are shown in Fig. 1-1. Maps of the 5 lakes and their respective watersheds showing subwatershed boundaries and the location of hydrological gauging equipment are shown in Fig. 4-1 (Hannah and Middle Lakes), Fig. 4-2 (Clearwater and Lohi Lakes) and Fig. 4-3 (Nelson Lake). There are 10 gauged watersheds in the study, 5 of which are lake outflows. The other 5 are headwater streams (although they do have beaver ponds in their basins).

The bedrock and surficial geology of the watersheds is described in Appendix 2. Table A2c-6 shows that exposed bedrock comprises the majority of the watershed areas of Hannah, Middle, Clearwater and Lohi Lakes. Forest cover is very sparse and exists only in the discontinuous soil pockets between the areas of exposed bedrock. The watershed of Nelson Lake has little exposed bedrock and is forested with white birch, jack pine, red pine, poplar and black spruce.

Drainage areas for the watersheds of the 5 lakes are given in Table 4-1. Hannah Lake drains via Middle Lake into Junction Creek, then via the Vermillion and Spanish Rivers ultimately into the North Channel of Lake Huron. Clearwater Lake drains into Lohi Lake and via Long Lake to Lake Panache and ultimately into the North Channel of Lake Huron. Nelson Lake also drains into the North Channel via Nelson Creek, the Vermillion and Spanish Rivers.

The Hydrological Atlas of Canada (1978) gives the long-term mean annual precipitation to the area as 0.8 - 0.9 m. Sudbury A, the closest meteorological station with long-term mean precipitation data, reports the annual mean to be 0.835 m, of which 0.213 m falls as snow (water equivalent). The long-term mean annual unit runoff has been reported as 0.3 - 0.4 m yr^{-1} (Hydrological Atlas of Canada 1978) and 0.38 - 0.45 m yr^{-1} (Pentland 1968). Based on a network of pan evaporation data, the long-term mean annual lake evaporation is estimated at 0.5 - 0.6 m yr^{-1} (Hydrological Atlas of Canada 1978).

C. Results and Discussion

i. Precipitation

Precipitation falling on the lake surface after formation of ice cover is an input to the water balance of the following year, assuming that no exchange occurs with the lake during the period of ice cover. Thus, precipitation from Nov. 26, 1977 to Nov. 22, 1978

Table 4-1. Drainage areas (m^2 10^4) for the watersheds of Hannah, Middle, Clearwater, Lohi and Nelson Lakes. Areas of subwatersheds are also given as % of total watershed area and % total watershed gauged is given.

Lake	Inlet	Terrestrial Basin Area Gauged m^2 10^4		Terrestrial Basin Area Ungauged m^2 10^4		Lake Area m^2 10^4		Total Watershed Area m^2 10^4	% gauged
Hannah		0	0	76.3	73.6	27.3	26.4	103.6	26.4
Middle	Hh	103.6	37.7	142.8	52.0	28.2	10.3	274.6	48.0
Clearwater	1	90.5	21.6	224.8	53.7	76.5	18.3	418.6	46.3
	2	26.8	6.4						
Lohi	Cr	418.6	75.1	98.4	17.7	40.5	7.3	557.5	82.4
Nelson	1	104.9	9.5	567.8	51.2	309	27.9	1108	48.8
	2	44.3	4.0						
	3	81.7	7.4						

(effective water year for 1978) was included in the 1978 water balance. The 1979 water balance includes precipitation from Nov. 22, 1978 to Dec. 6, 1979 (effective water year for 1979). As shown in Table 4-2, the depth of precipitation in the effective water year was less than that measured during the calendar year for lakes Hannah, Middle, Clearwater and Lohi in 1978. However, the reverse was true in 1979. At Nelson Lake, precipitation in the effective water year was greater than that in the calendar year for both 1978 and 1979. The differences in depth between the water year and calendar year for the 5 lakes were generally small, ranging from 1% to 7%.

As discussed in Appendix 3, the depth of precipitation at Nelson Lake, Hannah and Middle Lakes, and Clearwater and Lohi Lakes was measured at the Sudbury North (SN), Sudbury Center (SC) and Sudbury South (SS) stations respectively. The depth of precipitation was different at each station, being greatest at the SN station in both years. Compared to long-term records at Sudbury A, both 1978 and 1979 were drier than normal at the SS and SC stations whereas the SN station received more precipitation than normal.

The monthly depths of precipitation from June 1977 to December 1979 for the 10 gauged watersheds of the 5 lakes are plotted in Figures 4-4 to 4-13. In 1978, the temporal pattern was similar at all stations with maximum precipitation occurring in August and September and minimum precipitation in February and March. In 1979, April was the wettest month and February was dry except at the SN station. A localized storm occurred at this station in July making it the wettest month. The long-term records

Table 4-2. Depth of precipitation (m) recorded at 5 study lakes in 1978 and 1979 calendar years and effective water years (see text). Data for the long-term mean annual precipitation depth at Sudbury A meteorological station are included.

Lake	Precipitation Station	1978		1979		Long-term
		calendar year	water year	calendar year	water year	calendar year
Hannah	Sudbury Center	0.796	0.771	0.751	0.807	0.835
Middle	Sudbury Center	0.796	0.771	0.751	0.807	0.835
Clearwater	Sudbury South	0.775	0.759	0.772	0.833	0.835
Lohi	Sudbury South	0.775	0.759	0.772	0.833	0.835
Nelson	Sudbury North	0.885	0.893	0.986	1.011	0.835

for the Sudbury A meteorological station show September to be the wettest month and February the driest.

ii. Evaporation

Evaporation was calculated as the residual term in the energy balance equation.

$$LE = \frac{\Delta R - \Delta S}{1 + B} \qquad (4\text{-}2)$$

where: LE = latent heat exchange between the lake surface and the atmosphere where L = latent heat of vapourization (590 cal gm^{-1}) and E = water vapour exchange

ΔR = net radiation at lake surface

ΔS = change in heat storage in lakewater

B = Bowen ratio

= H/LE where H = sensible heat exchange between the lake surface and the atmosphere

The terms of the energy balance for the 5 study lakes are described and presented in Appendix 3. Lake evaporation rates estimated in this manner ranged from 0.52 m yr^{-1} to 0.76 m yr^{-1} in 1978 (Table 4-3) and from 0.54 m yr^{-1} to 0.71 m yr^{-1} in 1979 with the lowest rate occurring in Nelson Lake and the highest rate in Middle Lake in both years. The long-term mean annual evaporation rate for the area is 0.5 m yr^{-1} to 0.6 m yr^{-1} (Hydrological Atlas of Canada 1978).

Not only do the annual rates differ from lake to lake, but the monthly pattern of evaporation differs as well (Fig. 4-14 to 4-18). At Hannah and Middle Lakes, evaporation was at a maximum in

Table 4-3. Annual lake evaporation (m yr^{-1}) for the 5 study lakes for 1978 and 1979.

Lake	Annual Evaporation (m yr^{-1}) 1978	1979
Hannah	0.722	0.682
Middle	0.755	0.706
Clearwater	0.626	0.609
Lohi	0.635	0.654
Nelson	0.521	0.535

June and July then declined steadily from August through November. The evaporation rate in May was near the June and July maxima. By contrast, there was net condensation on Nelson Lake in May and evaporation rates peaked in September. The October and November evaporation rates at Nelson Lake were twice those at Hannah and Middle Lakes. Clearwater and Lohi Lakes showed patterns intermediate between these two, with low evaporation rates in May, peak values in June, July and August and steadily declining rates from September through November.

The rate of evaporation is essentially governed by two factors. There must be a sufficient supply of energy to provide the latent heat of vapourization so that water molecules may escape the surface and there must be a mechanism (wind) to remove the vapour so that a vapour pressure gradient exists above the surface. The monthly patterns observed may be explained by contrasting Middle and Nelson Lakes, assuming that the radiation input per unit area at Middle and Nelson Lakes were identical. Table 4-4 shows that the net radiation per unit area was similar at the two lakes. In the spring and early summer, a greater amount of heat per unit area was stored in Nelson Lake than in Middle Lake (Table 4-4). Consequently, the outgoing latent and sensible heat fluxes were smaller at Nelson Lake and evaporation rates were lower. In the fall, the converse was true (Table 4-4). The large negative ΔS values for Nelson Lake show that a greater amount of heat was lost per unit area of Nelson Lake than in Middle Lake and consequently the latent and sensible heat loss was greater at Nelson Lake. The net result was that evaporation rates in the fall were higher at Nelson Lake than at Middle lake. Although these patterns are quite

Table 4-4: Net radiation (ΔR), change in heat storage in the lake (ΔS), sensible (H) and latent (LE) heat exchanges in cal cm^{-2} day^{-1} for Middle and Nelson Lakes for selected spring and fall periods in 1978 and 1979. Negative ΔS vales denote heat loss by lake. Negative LE values denote condensation on the lake.

	Date	ΔR (cal cm^{-2} day^{-1})	ΔS (cal cm^{-2} day^{-1})	H (cal cm^{-2} day^{-1})	LE (cal cm^{-2} day^{-1})
	Spring				
Middle	25/5/78–28/5/78	478	49	-125	553
Nelson	24/5/78–29/5/78	479	712	147	-380
Middle	29/5/78–4/6/78	316	-49	69	296
Nelson	30/5/78–6/6/78	342	169	37	135
Middle	5/6/78–13/6/78	378	-7.2	77	308
Nelson	7/6/78–12/6/78	309	217	19	73
Middle	16/5/79–23/5/79	373	48	27	299
Nelson	16/5/79–21/5/79	390	980	247	-838
Middle	24/5/79–29/5/79	311	12	69	231
Nelson	22/5/79–27/5/79	328	-28	49	307
Middle	30/5/79–5/6/79	438	64	29	345
Nelson	28/5/79–3/6/79	395	521	44	-169
Middle	6/6/79–12/6/79	380	38	47	265
Nelson	4/6/79–13/6/79	382	408	-0.6	-25
	Fall				
Middle	28/9/78–1/10/78	77	-4	27	54
Nelson	26/9/78–2/10/78	87	-308	137	258
Middle	2/10/78–12/10/78	100	-19	40	80
Nelson	3/10/78–10/10/78	77	-275	130	223
Middle	13/10/78–15/10/78	136	-137	114	158
Nelson	11/10/78–16/10/78	146	-437	210	374
Middle	24/9/79–1/10/79	186	21	33	132
Nelson	25/9/79–2/10/79	186	169	2.4	15
Middle	2/10/79–10/10/79	87	-86	61	111
Nelson	3/10/79–8/10/79	72	-695	270	498
Middle	11/10/79–17/10/79	79	-58	55	81
Nelson	9/10/79–14/10/79	74	-599	279	394

consistent for both 1978 and 1979, the occasional anomaly occurs, perhaps because single-site temperature profiles may not have been sufficient to characterize the temperature structure of a lake the size of Nelson Lake (E. Robertson, pers. comm. 1980).

The effect that heat storage by a lake has on the evaporation rate is illustrated in Fig. 4-19, a plot of the fraction of net radiation lost as latent heat flow (LE/ΔR) for Middle and Nelson Lakes in 1978 and 1979. At Middle Lake, the fraction is roughly constant (~0.8) from May to October and increases in November. At Nelson Lake, the fraction is lower in the spring and early summer (-0.7 to 0.2) and increases steadily to peak in November. Comparing the two lakes, the LE/ΔR values are lower for Nelson Lake than for Middle Lake in May and June because Nelson Lake stores more heat per unit area. From September through November, Nelson Lake gives off more heat per unit area than Middle Lake and the LE/ΔR values are higher. Similar observations were made by Barry and Robertson (1977), who used energy budget calculations to compare the evaporation rates of three lakes near Chalk River, Ontario, which had a range of surface area and lake volume.

iii. Surface Runoff

The mean daily discharge values for the 10 gauged streams are given in Appendix 3 in Tables A3-5 to A3-34. The minimum, maximum and mean values of the mean daily discharges are summarized in Table 4-5. The range of mean daily flow within a year is large for each stream. In 1978, 7 of 10 streams were dry in the summer. The maximum range of flow was 53.8 L sec^{-1} to 631 L sec^{-1} in the Nelson Lake outlet and the minimum range of 0 to 56.6 L sec^{-1} in Clearwater inlet 2. In 1979, 8 of 10 streams were dry in the summer

Table 4-5. Minimum, maximum and mean values of mean daily discharge (L sec^{-1}) and the ratio of maximum mean daily discharge to average mean daily discharge for the gauged streams in 1978 and 1979.

Stream	Year	Minimum Discharge	Maximum Discharge	Mean Discharge	Maximum/mean
Clearwater 1	1978	0	202	12.7	15.9
	1979	0	446	19.7	22.7
Clearwater 2	1978	0	56.6	3.47	16.3
	1979	0	96.2	5.72	16.8
Nelson 1	1978	0.49	201	18.0	11.2
	1979	1.31	392	25.3	15.5
Nelson 2	1978	0	133	8.11	16.4
	1979	0	204	10.7	19.1
Nelson 3	1978	1.41	99.7	12.2	8.2
	1979	0.99	232	19.7	11.8
Hannah Outlet	1978	0	89.9	11.8	7.6
	1979	0	139	16.0	8.7
Middle Outlet	1978	0	325	35.2	9.2
	1979	0	376	44.6	8.4
Clearwater Outlet	1978	0	400	48.0	8.3
	1979	0	484	66.8	7.3
Lohi Outlet	1978	0	392	65.4	6.0
	1979	0	528	86.6	6.1
Nelson Outlet	1978	53.8	631	172	3.7
	1979	0	1390	227	6.1

with the maximum flow range again recorded at the Nelson Lake outlet (0 to 1390 L sec^{-1}). The minimum range was 0 to 96.2 L sec^{-1} in Clearwater inlet 2. Another way of expressing the range in flow is as a ratio of the maximum mean daily flow to the average mean daily flow over the year. In 1978, these values ranged from 3.7 to 16.4 and in 1979 the range was 6.1 to 22.7 (Table 4-5) In both 1978 and 1979, the mean value of this ratio for the 5 headwater streams (13.6 in 1978 and 17.2 in 1979) was significantly greater (t-test $p =$ 0.05) than the mean of the 5 lake outlets (7.0 in 1978 and 7.3 in 1979). The lower values at the lake outlets are a reflection of the damping effect that lake storage has on the extremes of streamflow.

Annual unit runoff values (the depth of water draining a unit area of watershed per year) are summarized in Table 4-6. In 1978, values ranged from 0.358 m yr^{-1} to 0.577m yr^{-1}. In 1979, the range was 0.486 m yr^{-1} to 0.760 m yr^{-1}. To factor out the effect of precipitation depth on unit runoff, we have also expressed the data as annual unit yield (annual unit runoff/annual precipitation depth as %). Unit yield is the % of annual precipitation received by a watershed which is lost to runoff. Conversely, 100% minus the unit yield is the % of precipitation received by a watershed lost to evapotranspiration, assuming no change in storage by the basin. Unit yield ranged from 45% to 65% in 1978 and 64% to 89% in 1979. The higher 1979 values can be explained in part by the fact that a greater proportion of the annual precipitation fell during the winter and spring months and subsequently contributed to spring runoff. In 1979, 34% to 44% of the annual precipitation fell from January to April at the 5 lakes compared to only 22% to 25% for

Table 4-6. Annual unit runoff (m yr^{-1}) and unit yield (%) (annual unit runoff/annual precipitation) for the gauged watersheds in 1978 and 1979.

Watershed	1978 unit runoff (m yr^{-1})	1978 unit yield (%)	1979 unit runoff (m yr^{-1})	1979 unit yield (%)
Clearwater 1	0.443	57	0.685	89
Clearwater 2	0.408	53	0.673	87
Nelson 1	0.541	61	0.760	77
Nelson 2	0.577	65	0.760	77
Nelson 3	0.471	53	0.759	77
Hannah Outlet	0.358	45	0.486	65
Middle Outlet	0.404	51	0.513	68
Clearwater Outlet	0.361	47	0.503	65
Lohi Outlet	0.370	48	0.490	64
Nelson Outlet	0.490	55	0.646	66

the comparable time period in 1978. Snowmelt and spring rains are a highly efficient source of runoff because the ground is either frozen or saturated and losses to evapotranspiration are minimal (Pentland 1968). The long-term mean annual unit runoff for the greater Sudbury area has been estimated at 0.3 m yr^{-1} to 0.4 m yr^{-1} (Hydrological Atlas of Canada 1978) and at 0.38 m yr^{-1} to 0.45 m yr^{-1} (Pentland 1968). Expressed as a percentage of the long-term annual precipitation (0.8 to 0.9 m yr^{-1}) or as a unit yield, these figures could range from 33% to 50% and 35% to 56% respectively. Our 1978 values lie at the high end of these ranges but the 1979 values are all above the range. The higher unit yield measured at our study watersheds compared to the long-term mean unit yields for the greater Sudbury area may be related to the relative lack of forest cover in our basins. Reviews by Hibbert (1967) and Anderson _et_ _al_. (1976) show that annual unit runoff generally increases after a reduction in forest cover due to cutting. In our study basins, forest cover was reduced probably as a result of SO_2 fumigation due to local smelting operations. In Chapter 3 of this report, Dillon and Smith showed that this probably occured 40-50 years ago.

The variability in yield between our 10 watersheds is reduced if lake outlets are considered separately from headwater basins. In both 1978 and 1979, the mean unit yield for the 5 lake outlets (49.2% and 65.6% respectively) was significantly less (t-test, $\rho = 0.05$) than the mean unit yield for the 5 headwater streams (57.8% and 81.4% respectively). These results imply that evapotranspiration rates for watersheds containing lakes are higher than those for headwater basins. This in turn implies that the lake evaporation rate is greater than the terrestrial evapotranspiration rate, as originally indicated by Penman (1948). If annual evapotranspiration is calculated as the difference between precipitation and runoff, a comparison between the two can be made (Table 4-7). The data show that in both 1978 and 1979, mean annual lake evaporation ($0.65\ \mathrm{m\ yr^{-1}}$ and $0.64\ \mathrm{m\ yr^{-1}}$ respectively) was significantly (t-test, $\rho = 0.05$) greater than mean annual evapotranspiration ($0.35\ \mathrm{m\ yr^{-1}}$ and $0.17\ \mathrm{m\ yr^{-1}}$ respectively) for the 5 headwater basins. The reasons for this are probably twofold. First, there is a constant moisture supply available for lake evaporation whereas the soils would not always be saturated with water thereby preventing evapotranspiration from proceeding at its maximum rate. Secondly, it is probably windier over the exposed lake surface than the terrestrial basin, causing a greater vapour pressure gradient over the lake and promoting higher evaporation rates.

In 1979, the mean unit yield for the two inlet streams of Clearwater Lake was 88%, significantly different (t-test, $\rho = 0.05$) than the mean value (77%) of the three inlet streams of Nelson Lake. This observation suggests that there is greater evapotranspiration from the forested Nelson basins than the Clearwater basins, where about 90% of the basins are exposed bedrock and forest growth is sparse. However, there was no significant difference (t-test, $\rho = 0.05$) in unit yield between the Clearwater and Nelson watersheds in 1978 and we conclude that there is insufficient evidence to support the hypothesis. Based on these results, we have used the mean unit yield of the 5 headwater basins to estimate runoff from the ungauged areas of the terrestrial basin (Appendix 3).

Monthly unit runoff and precipitation depth for the 10 gauged watersheds are plotted in Figs. 4-4 to 4-13. The general pattern of

Table 4-7. Annual evapotranspiration (precipitation-runoff in m yr^{-1}) for the 5 headwater basins and annual lake evaporation (m yr^{-1}) in 1978 and 1979.

Basin	Annual Evapotranspiration (m yr^{-1}) 1978	1979
Clearwater 1	0.333	0.087
Clearwater 2	0.367	0.099
Nelson 1	0.345	0.226
Nelson 2	0.308	0.225
Nelson 3	0.414	0.226
mean	0.353	0.173

Lake	Annual Evaporation (m yr^{-1}) 1978	1979
Hannah	0.722	0.682
Middle	0.755	0.706
Clearwater	0.626	0.609
Lohi	0.635	0.653
Nelson	0.521	0.535
mean	0.652	0.637

runoff is basically similar for each stream. Peak values occur in the spring (March, April, May) as a response to snowmelt. Runoff decreases after the spring pulse as vegetation comes into leaf and evapotranspiration increases. There is a secondary peak of runoff in the fall (October, November) as the vegetation becomes dormant, evapotranspiration decreases and the moisture content of the soil increases. Runoff is generally low in the winter as precipitation is stored as snow. The timing of this pattern varied slightly between the two study years and between streams. In 1978, the fall peak occurred in October, whereas it occurred in November in 1979. Spring peak flow for the inlets to Nelson Lake tended to be 7-10 days later than the peak values for the Hannah, Middle, Clearwater and Lohi streams. The peak flow at the Nelson outlet was later still.

An overall mean (10 watersheds) of 71% of the total annual flow (Table 4-8) occurred in the months of March, April and May in 1979 (range 54% - 86%), significantly greater (t-test, $\rho = 0.05$) than the mean value of 53% in 1978 (range 33% - 68%). This reflects the fact that a greater fraction of the annual precipitation fell in the winter and spring months in 1979. Peak mean daily discharge values were correspondingly higher in 1979, with values for the Nelson Lake outlet, Nelson inlet 3 and Clearwater inlet 1 being more than twice the 1978 peak flows (Table 4-5). There was no significant difference (t-test, $\rho = 0.05$) in spring flow/annual flow between the 5 lake outlets and the 5 headwater streams in either 1978 or 1979.

Although there are insufficient data to attempt to relate streamflow characteristics to watershed properties (see for example Thomas and Benson 1970), the data show that lake outlets have different hydrological responses than headwater streams. The 5 lake

Table 4-8. % total annual flow occurring in each month for the gauged watersheds in 1978 and 1979.

Watershed	J	F	M	A	M	J	J	A	S	O	N	D
					1978							
Clearwater 1	3.4	1.7	2.0	45.7	10.3	2.2	0.5	0.8	8.3	15.8	6.6	2.6
Clearwater 2	1.3	1.2	4.1	46.6	12.7	0.6	0.1	2.3	11.8	12.7	5.3	1.2
Nelson 1	4.1	2.0	1.5	24.0	27.8	1.0	0.7	2.6	6.1	16.9	9.4	3.9
Nelson 2	1.8	0.9	0.7	34.8	23.3	0.5	0.5	2.3	7.7	20.1	5.4	2.0
Nelson 3	3.0	2.9	2.1	17.6	25.4	3.7	1.8	3.0	4.2	20.3	9.3	6.6
Hannah Outlet	5.7	3.3	3.2	34.5	19.6	3.3	0.2	0.0	1.8	16.6	5.3	6.4
Middle Outlet	9.8	7.3	7.1	31.7	13.9	1.2	0.1	0.1	3.2	15.5	5.3	4.6
Clearwater Outlet	5.8	3.6	3.5	33.1	19.2	3.1	0.3	0.0	3.8	17.1	4.7	5.8
Lohi Outlet	8.5	4.5	4.0	27.3	21.8	4.3	0.5	0.0	2.9	14.2	5.8	6.2
Nelson Outlet	8.2	5.2	3.7	6.3	23.4	11.7	5.7	3.8	3.7	11.7	8.6	8.0
					1979							
Clearwater 1	1.5	1.1	22.1	46.1	7.8	0.4	0.1	0.0	0.9	4.6	9.5	5.9
Clearwater 2	0.6	1.1	27.2	35.1	7.5	0.5	0.0	0.0	2.0	5.1	12.9	8.0
Nelson 1	1.4	1.4	7.0	42.5	13.0	2.1	4.5	1.0	1.2	7.4	12.0	6.4
Nelson 2	0.4	0.3	13.4	44.9	10.2	1.2	0.1	1.0	1.2	8.0	13.0	6.3
Nelson 3	4.0	2.6	8.2	35.8	14.3	3.0	7.6	1.2	1.3	6.3	10.1	5.5
Hannah Outlet	4.7	3.2	22.6	44.9	18.4	1.4	0.0	0.0	0.0	0.0	0.1	4.6
Middle Outlet	4.1	2.9	23.5	40.9	17.6	1.0	0.0	0.0	0.0	0.0	2.8	7.2
Clearwater Outlet	4.2	3.2	17.4	41.9	18.3	2.3	0.1	0.0	0.0	0.0	2.9	9.7
Lohi Outlet	4.9	3.6	15.4	40.8	23.0	3.1	0.2	0.0	0.0	0.0	1.0	7.9
Nelson Outlet	5.3	3.5	5.1	21.0	27.8	11.2	4.0	0.0	0.0	0.5	10.0	11.6

outlets had significantly ($\rho = 0.05$) lower unit yields and ratios of peak flow/mean flow than the headwater basins in both 1978 and 1979. Neither is there sufficient statistical evidence to show that the 5 headwater streams are different amongst themselves. However, it is interesting to note that Nelson inlet 3, the basin with the greatest amount of surficial material (Appendix 2), had the lowest unit yield (and hence the greatest evapotranspiration rate), the lowest ratio of spring flow/annual flow and the lowest ratio of peak flow/mean flow of the 5 headwater basins. The greater amount of surficial material in the basin may influence the hydrological characteristics by increasing the storage potential. The storage potential is reflected in the fact that Nelson inlet 3 had the highest ratio of baseflow/total flow (Table 4-9), baseflow being the component of streamflow that sustains flow in dry weather periods. Annual baseflow was calculated as the sum of the monthly baseflows, which were approximated as the lowest recorded flow in the month. Greater storage may lead to higher evapotranspiration, by increasing soil moisture content, resulting in decrease unit yield. Greater storage would also tend to reduce peak flow in the same manner as storage potential by lakes. The storage sustained flow in Nelson 3 through the summer months whereas 3 of the other headwater streams were dry in the summer.

All 5 headwater streams had ponds in their drainage basins created by beavers. On several occasions, the beaver dams broke and the ponds emptied quickly. The greatest flow occurred at Nelson inlet 3 when a beaver dam broke on July 26, 1979 following heavy rains on the previous day. The volume of water was estimated at $3.95\ 10^4\ m^3$, 6.3% of the annual flow of the stream and approximately equal to the remainder of the discharge that occurred from June - September of that year.

Table 4-9. Ratio of baseflow to total annual flow for the 5 headwater basins in 1978 and 1979.

Watershed	1978	1979
Clearwater 1	0.229	0.235
Clearwater 2	0.170	0.208
Nelson 1	0.286	0.334
Nelson 2	0.160	0.424
Nelson 3	0.336	0.561

iv. Groundwater

Ground water typically enters lakes through the littoral zone and leaves through the lake bed (Winter 1978). Generally, there is a net gain of ground water by lakes in areas where precipitation is greater than evapotranspiration and ground water levels are close to the surface. The paucity of surficial material in our study watersheds makes it unlikely that ground water is an important component in the lake water balance and we have assumed it to be negligible. No measurements were made to substantiate this assumption. In fact, few measurements have been made to quantify the importance of ground water to the water balance of Shield lakes. Ground water is commonly estimated as the residual term in the water balance of the lake but this is unsatisfactory because it includes the errors inherent in the other components. Schindler et al (1976) reported that ground water flow (estimated from a network of peizometers and wells) to Rawson Lake, N.W. Ontario was negligible.

v. Storage

Annual changes in lake level and thus storage were generally small for the 5 lakes (Tables 4-10 to 4-14). As a % of the total water supply to the lake, the change in storage ranged from 0.3% to 3.0% except for Hannah Lake in 1978 (7.0%). There was a net loss of water from Hannah, Middle and Nelson Lakes in 1978 and a net gain in all other cases.

vi. Water Balance of Lakes

The annual water balances for 1978 and 1979 for Hannah, Middle, Clearwater, Lohi and Nelson Lakes are presented in Tables 4-10 to 4-14 respectively. In computing these balances, each supply

Table 4-10. Summary of annual water balances for Hannah Lake, 1978 and 1979.

		Supply to lake				Loss from Lake			ΔStorage		Balance=supply-loss±Δstorage		
		$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	% (b)		$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	% (c)	$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	% (d)
1978	Ungauged runoff	35.11	1.286	62.5	Outlet	37.10	1.359	65.3	-4.12	-0.151	3.48	0.127	6.2
	Precipitation	21.06	0.771	37.5	Evaporation	19.71	0.722	34.7					
	Total	56.17	2.057	100	Total	56.81	2.081	100					
1979	Ungauged runoff	46.62	1.708	67.9	Outlet	50.35	1.844	73.0	0.57	0.021	-0.88	-0.032	-1.3
	Precipitation	22.04	0.807	32.1	Evaporation	18.62	0.682	27.0					
	Total	68.66	2.515	100	Total	68.97	2.526	100					

(a) calculated as $m^3\ yr^{-1}/m^2$ lake surface
(b) calculated as % total supply
(c) calculated as % total loss
(d) calculated as % $\frac{\text{supply + loss}}{2}$

Table 4-11. Summary of annual water balances for Middle Lake, 1978 and 1979.

		Supply to lake				Loss from Lake			ΔStorage		Balance=supply-loss±Δstorage		
		$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	%(b)		$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	%(c)	$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$(a)	%(d)
1978	Hannah outlet	37.10	1.316	29.8	Outlet	110.9	3.933	83.9	-1.69	-0.060	-5.91	-0.211	-4.6
	Ungauged runoff	65.71	2.330	52.7	Evaporation	21.28	0.755	16.1					
					Total	132.2	4.688	100					
	Precipitation	21.75	0.771	17.5									
	Total	124.6	4.417	100									
1979	Hannah outlet	50.35	1.785	31.4	Outlet	140.7	4.989	87.6	0.59	0.021	-0.79	-0.030	-0.5
					Evaporation	19.90	0.706	12.4					
	Ungauged runoff	87.25	3.094	54.4	Total	160.6	5.695	100					
	Precipitation	22.77	0.807	14.2									
	Total	160.4	5.686	100									

(a) calculated as $m^3\ yr^{-1}/m^2$ lake surface
(b) calculated as % total supply
(c) calculated as % total loss
(d) calculated as % $\frac{\text{supply + loss}}{2}$

Table 4-12. Summary of annual water balances for Clearwater Lake, 1978 and 1979.

		Supply to lake				Loss from Lake			ΔStorage		Balance=supply-loss±Δstorage		
		$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (b)		$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (c)	$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	$10^6 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (d)
1978	Inlet 1	40.08	0.524	19.1	Outlet	151.2	1.976	75.9	5.81	0.076	4.89	0.064	2.4
	Inlet 2	10.94	0.143	5.2	Evaporation	47.87	0.626	24.0					
	Ungauged runoff	100.7	1.316	48.0	Total	199.1	2.602	99.9					
	Precipitation	58.08	0.759	27.7									
	Total	209.8	2.742	100									
1979	Inlet 1	62.02	0.811	21.8	Outlet	210.6	2.753	81.9	2.14	0.028	25.66	0.336	9.5
	Inlet 2	18.03	0.236	6.3	Evaporation	46.57	0.609	18.1					
	Ungauged runoff	141.2	1.846	49.5	Total	257.2	3.362	100					
	Precipitation	63.73	0.833	22.4									
	Total	285.0	3.726	100									

(a) calculated as $m^3\ yr^{-1}/m^2$ lake surface
(b) calculated as % total supply
(c) calculated as % total loss
(d) calculated as % $\frac{\text{supply + loss}}{2}$

Table 4-13. Summary of annual water balances for Loni Lake, 1978 and 1979.

		Supply to lake				Loss from Lake			ΔStorage		Balance=supply-loss±Δstorage		
		$10^6 m^3 yr^{-1}$	m yr^{-1}(a)	%(b)		$10^6 m^3 yr^{-1}$	m yr^{-1}(a)	%(c)	$10^6 m^3 yr^{-1}$	m yr^{-1}(a)	$10^6 m^3 yr^{-1}$	m yr^{-1}(a)	%(d)
1978	Clearwater Outlet	151.2	3.733	66.9	Outlet	206.3	5.094	88.9	0.57	0.014	-6.57	-0.162	-2.9
	Ungauged runoff	44.09	1.089	19.5	Evaporation	25.73	0.635	11.1					
					Total	232.0	5.729	100					
	Precipitation	30.75	0.759	13.6									
	Total	226.0	5.581	100									
1979	Clearwater Outlet	210.6	5.200	68.8	Outlet	273.0	6.741	91.2	1.46	0.036	5.24	0.128	1.7
	Ungauged runoff	61.81	1.526	20.2	Evaporation	26.47	0.654	8.8					
					Total	299.5	7.395	100					
	Precipitation	33.74	0.833	11.0									
	Total	306.2	7.559	100									

(a) calculated as $m^3 yr^{-1}/m^2$ lake surface
(b) calculated as % total supply
(c) calculated as % total loss
(d) calculated as % $\frac{\text{supply + loss}}{2}$

Table 4-14. Summary of annual water balances for Nelson Lake, 1978 and 1979.

		Supply to lake				Loss from Lake			ΔStorage		Balance=supply-loss±Δstorage		
		$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (b)		$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (c)	$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	$10^4 m^3 yr^{-1}$	$m\ yr^{-1}$ (a)	% (d)
1978	Inlet 1	56.76	0.184	8.3	Outlet	542.8	1.757	77.1	-11.43	-0.037	-5.07	-0.016	-0.7
	Inlet 2	25.57	0.083	3.7	Evaporation	161.0	0.521	22.9					
	Inlet 3	38.49	0.125	5.6	Total	703.8	2.278	100					
	Ungauged runoff	290.5	0.940	42.3									
	Precipitation	276.0	0.893	40.2									
	Total	687.3	2.225	100.1									
1979	Inlet 1	79.77	0.258	8.5	Outlet	715.2	2.315	81.2	13.29	0.043	49.61	0.160	5.4
	Inlet 2	33.67	0.109	3.6	Evaporation	165.2	0.535	18.8					
	Inlet 3	62.00	0.201	6.6	Total	880.4	2.850	100					
	Ungauged runoff	455.5	1.474	48.3									
	Precipitation	312.4	1.011	33.1									
	Total	943.3	3.053	100.1									

(a) calculated as $m^3\ yr^{-1}/m^2$ lake surface
(b) calculated as % total supply
(c) calculated as % total loss
(d) calculated as % $\frac{\text{supply + loss}}{2}$

and loss term was measured or estimated separately. No term was obtained as a residual and consequently, an exact balance was not achieved. The error in the balance is the net sum of the errors (not the sum of the absolute errors) of the individual supply and loss terms. All annual budgets balanced to within 10%, 7 of 10 budgets balanced to within 5% and the mean annual balance was 3.5%. Averaging the two years, the best balance was achieved for Lohi Lake (2.3%), as expected since it is the lake with the greatest fraction of its inputs measured (Table 4-1).

There was no consistent pattern in the error term of the balances. In 5 of 10 cases the error was positive, indicating that either the supply was too great or the loss too small, and in 5 of 10 cases negative. Two of the 5 positive errors occurred in 1978 and 3 in 1979. Three of the 5 lakes had a positive error one year and a negative error the next. These results demonstrate that there did not appear to be any systematic error in the water balances.

The fact that the water budgets balance reasonably well implies that the assumptions made and methods used to calculate the input from ground water and the ungauged areas are at least roughly correct. With respect to ground water, this suggests that the net gain or loss of ground water by the lakes is small. It also indicates that the annual unit yield for the ungauged areas is similar to that of the gauged basins. However, the lack of direct measurements renders these conclusions tenuous.

Terrestrial runoff supplied most of the water to each lake, ranging from 60% in Nelson Lake to 86% in Lohi Lake in 1978 and from 67% (Nelson lake) to 89% (Lohi Lake) in 1979. Correspondingly, precipitation directly to the lake surface ranged from 40% to 14%

(1978) and 33% to 11% (1979) of the total water supply. The values are in approximate proportion to the ratio of lake area to total basin area (Table 4-1) but are not exactly so because of the water loss to evapotranspiration in the terrestrial basin.

Loss to the outflow was the most important mechanism of water loss in all lakes ranging from 65% to 89% in 1978 and 73% to 91% in 1979. Evaporation losses ranged from 35% to 11% in 1978 and 27% to 9% in 1979, this loss being highest in Hannah Lake in both years and least in Lohi Lake.

vii. Residence and Flushing Times

The residence time of a lake is the length of time needed to displace a volume of water equivalent to the volume of the lake. The term is defined as either lake volume/total supply to the lake or lake volume/total loss from the lake. However, because a greater % of the total loss was gauged than the total supply for all 5 lakes (Tables 4-10 to 4-14), we calculate residence time as lake volume/total loss (units of years). Flushing time is calculated as lake volume/lake outflow (units of years) and is longer than residence time because loss to evaporation is not included.

Residence and flushing times for the 5 lakes are given in Table 4-15. These values are different than those previously published (eg. Dillon *et al*. 1979) because the previous estimates were based on long-term unit runoff data.

Table 4-15: Residence and flushing times (years) of the 5 study lakes for 1978 and 1979.

Lake	Residence Time (years) 1978	1979	Flushing Time (years) 1978	1979
Hannah	1.90	1.57	2.91	2.14
Middle	1.32	1.09	1.58	1.24
Clearwater	3.22	2.50	4.25	3.05
Lohi	1.08	0.83	1.21	0.92
Nelson	5.10	4.08	6.61	5.02

D. Summary

1. Hydrological data were obtained for Hannah, Middle, Clearwater, Lohi and Nelson Lakes for the period June 1977 to December 1979. Each component of the annual water balance of the lakes was measured or estimated separately (precipitation, surface runoff, loss via outflow, evaporation, groundwater, and change in lake storage). Balances to within 10% were achieved for the 1978 and 1979 calendar years, giving confidence in the use of the data for the construction of chemical mass balances.
2. From 11 to 40% of the annual water supply to the lakes was provided by precipitation directly to the lake's surface, the remainder provided by surface runoff. Surface runoff data showed that the 5 headwater basins had significantly different hydrological responses than the 5 lake outlets with respect to unit yield and peak flow/mean flow. The data also suggested that Nelson inlet 3 had different hydrological characteristics (unit yield, spring flow/annual flow, peak flow/mean flow, base flow/total flow) than the other headwater basins, because it had a greater amount of surficial material deposited in its basin.
3. From 65 to 91% of the annual water loss from the lakes was via the outlet, the remainder via evaporation. The monthly pattern of lake evaporation (as calculated by an energy balance) differed from lake to lake because of differing heat storage capacities.

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Figure 4-3. Drainage basin boundaries of Nelson Lake watersheds. R = site of streamflow monitoring station, P = site of precipitation gauge, S = site of lake level gauge.

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Figure 4-19. Fraction of net radiation (ΔR) received each month lost by evaporation (LE) from Middle Lake and Nelson Lake in 1978 and 1979.

Fig.4-1

Drainage basin boundaries.

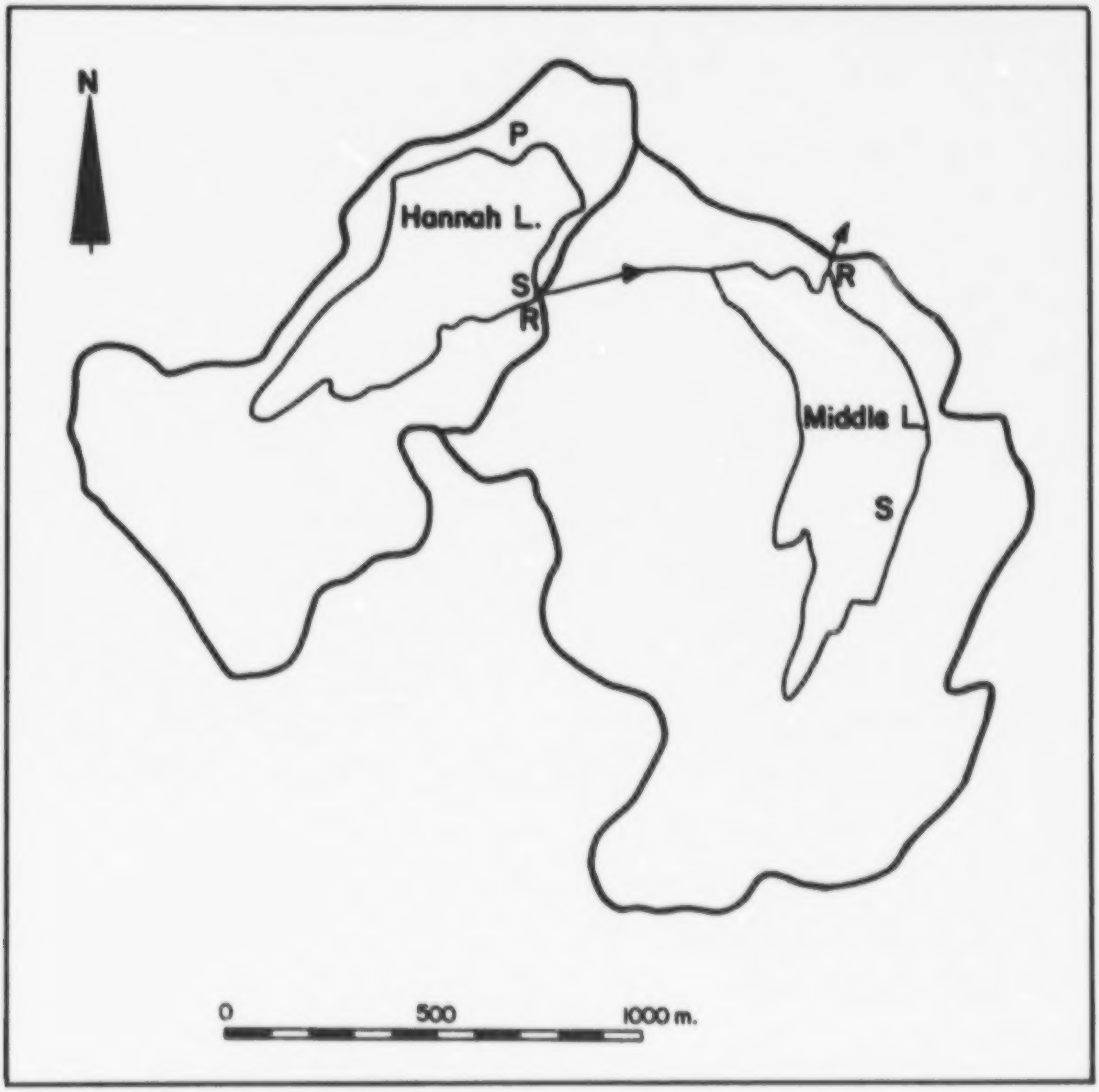


Fig.4-2

Drainage basin boundaries.

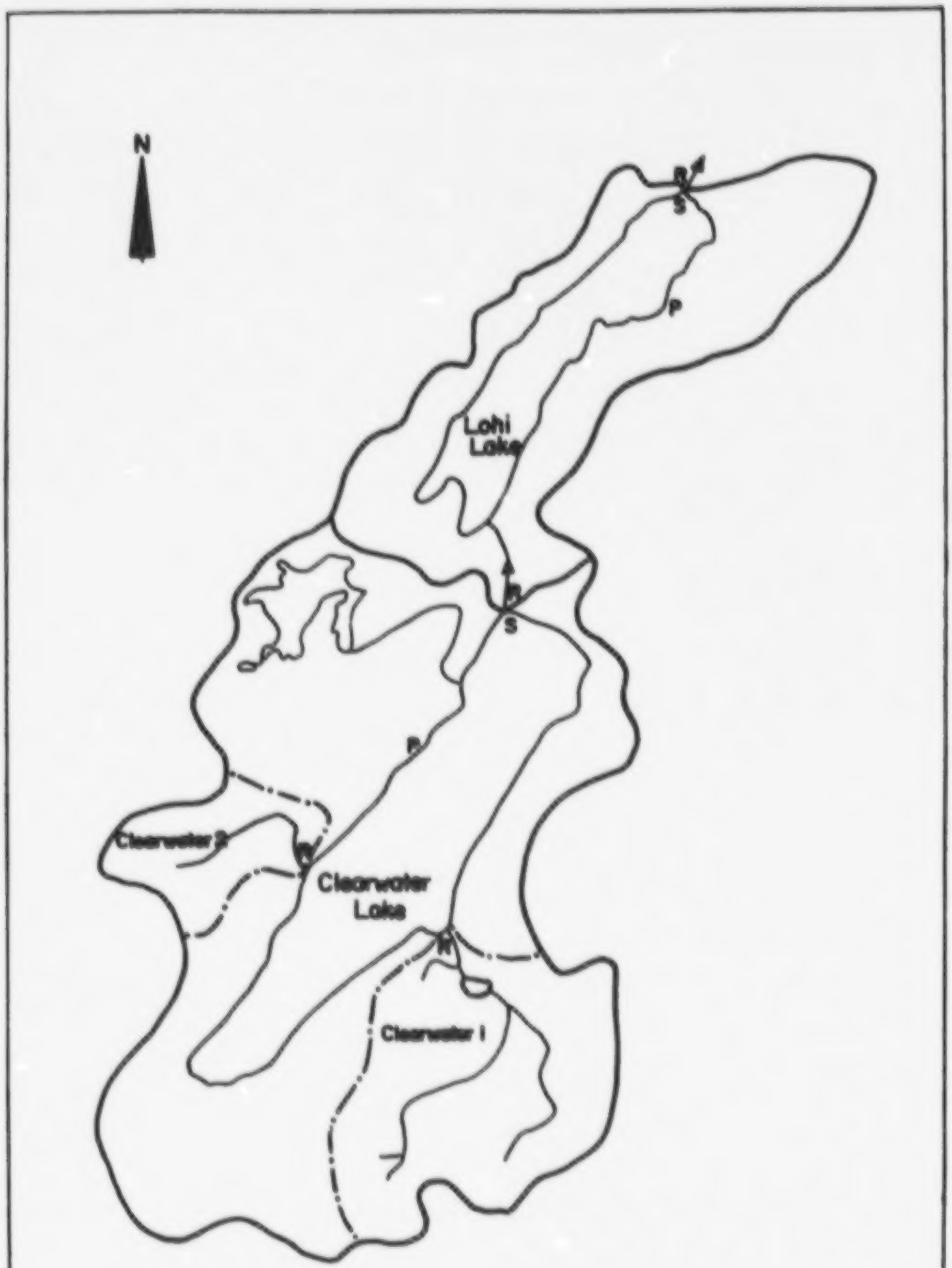


Fig.4-3

Drainage basin boundaries.

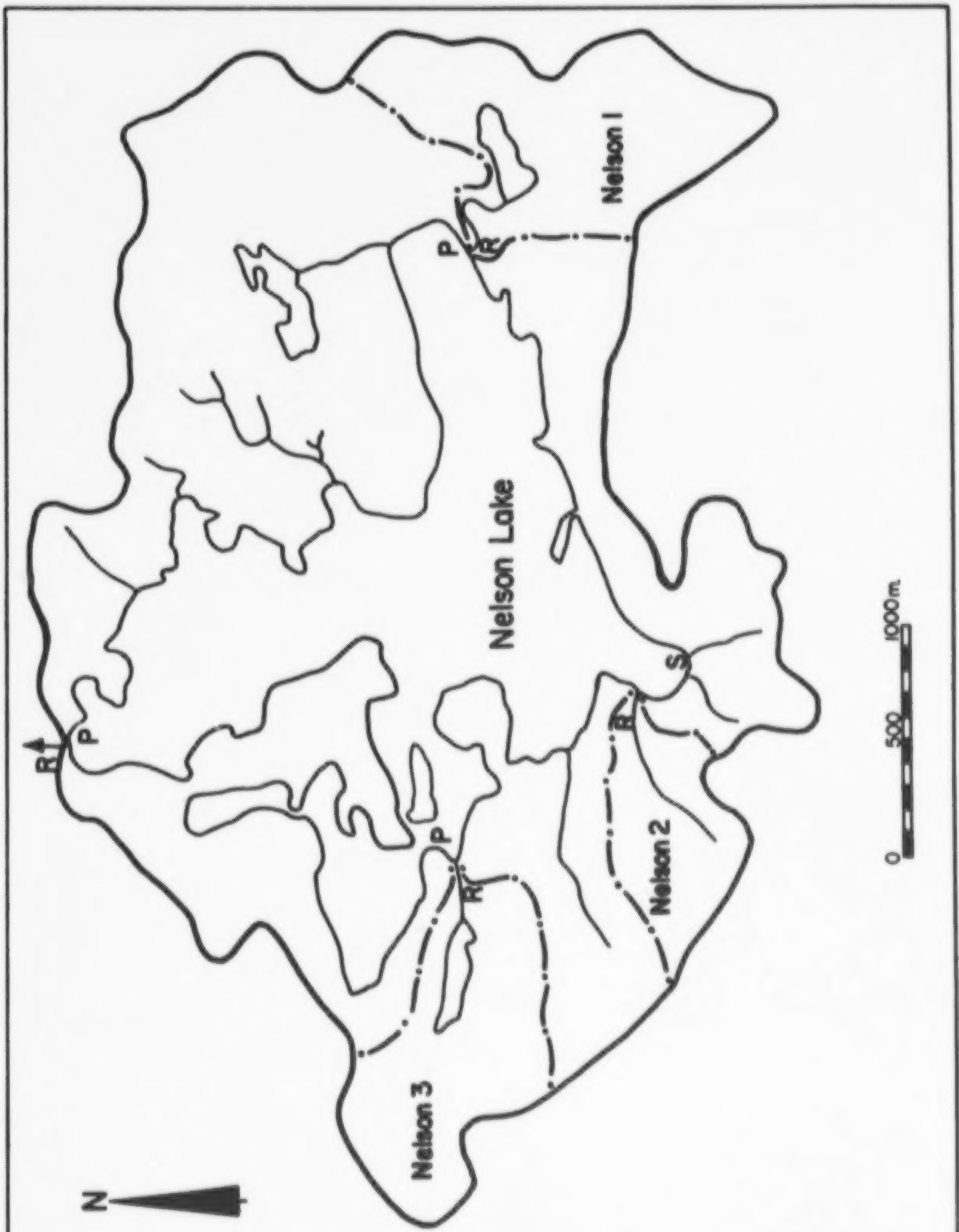


Fig.4-4

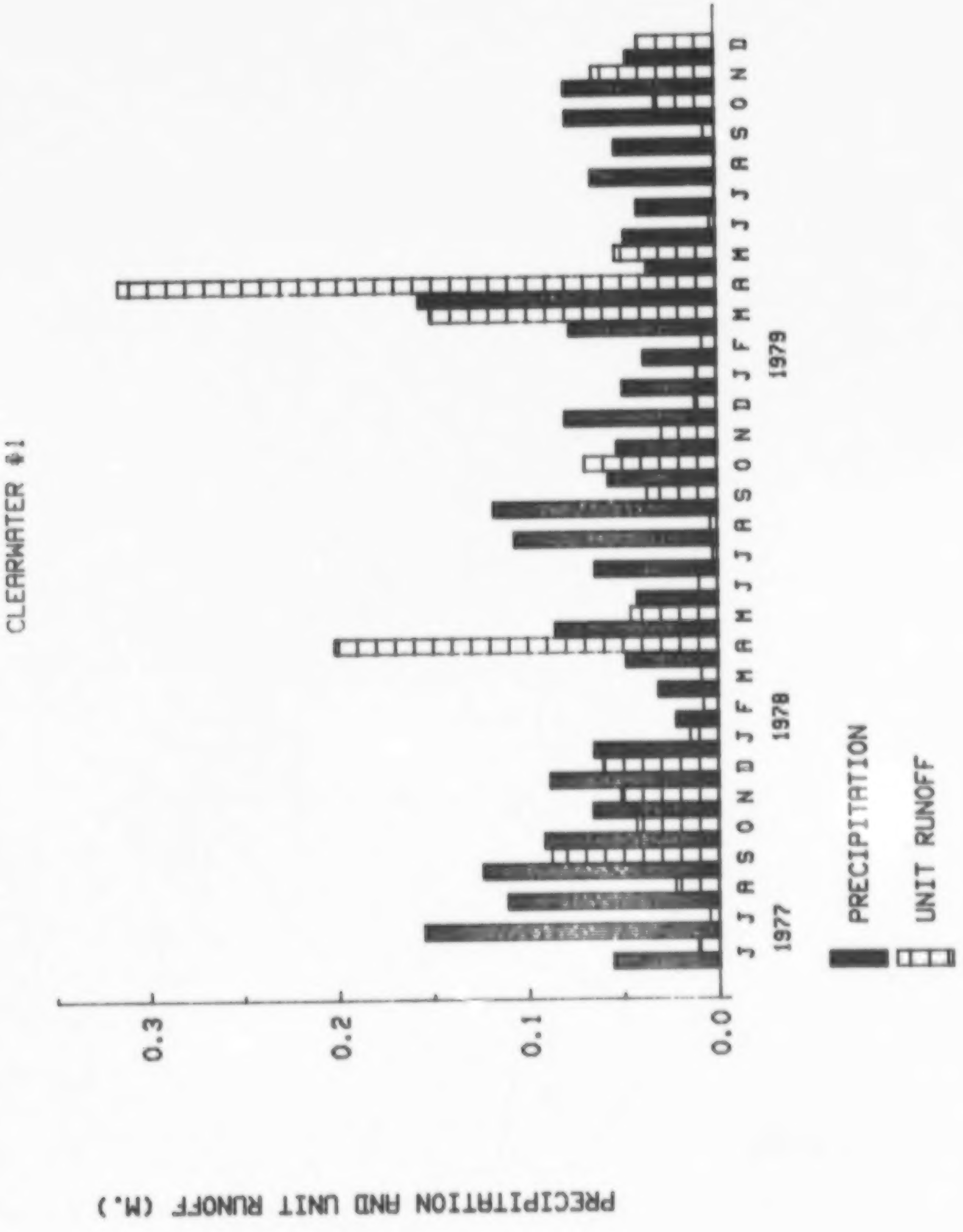
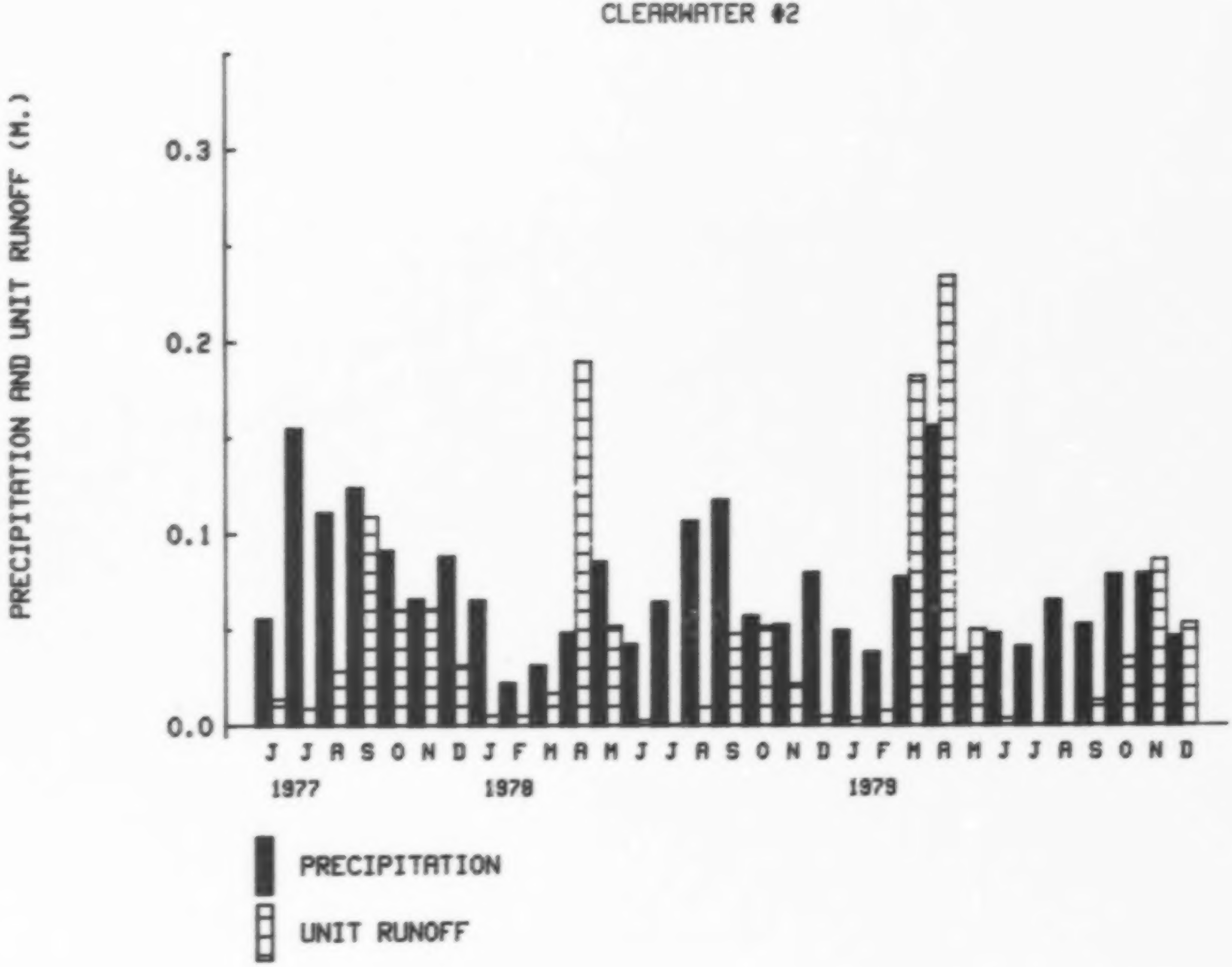

CLEARWATER #1
PRECIPITATION AND UNIT RUNOFF (M.)
0.0
0.1
0.2
0.3
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-5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0.3
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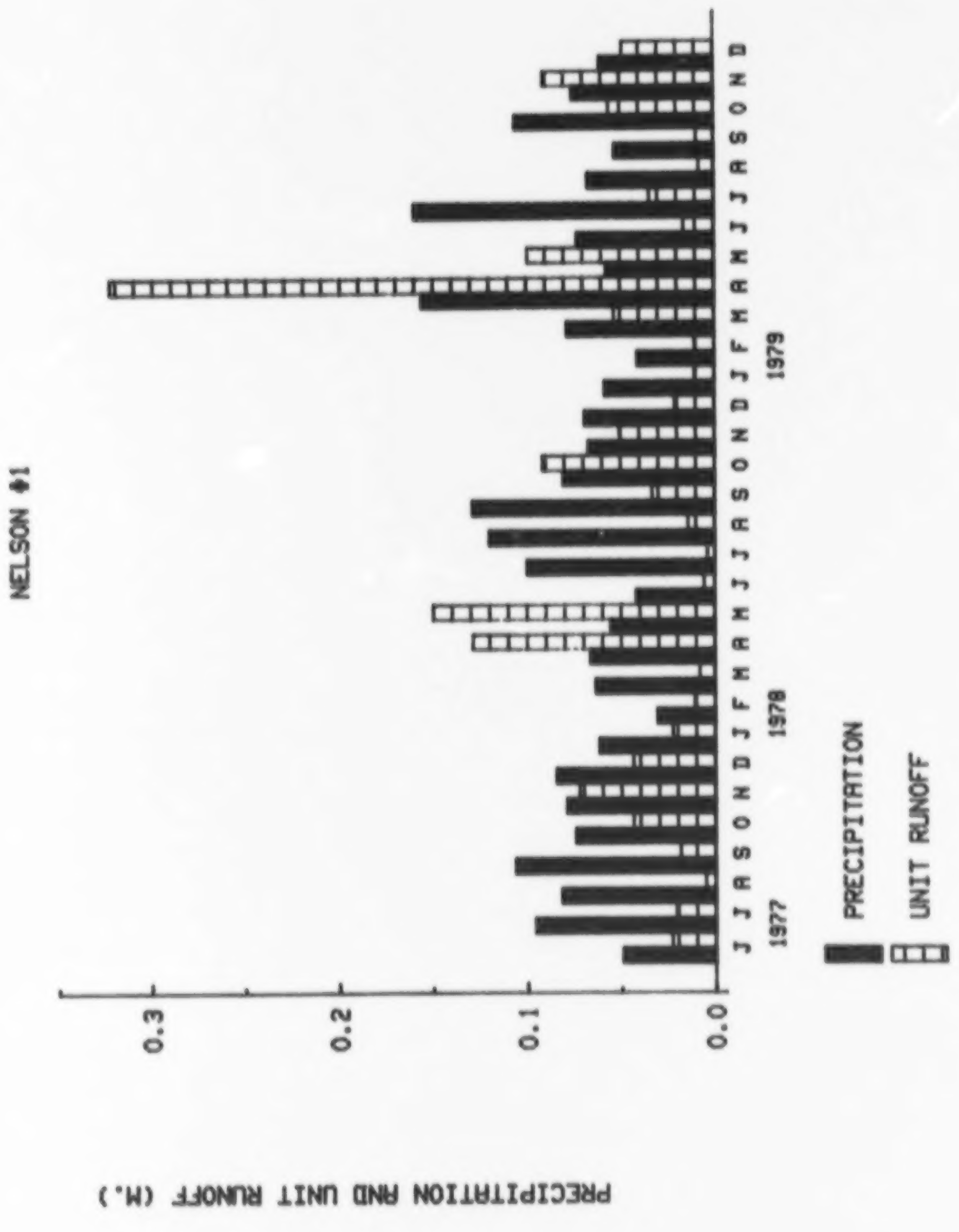
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-6


NELSON #1
PRECIPITATION AND UNIT RUNOFF (M.)
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0.1
0.2
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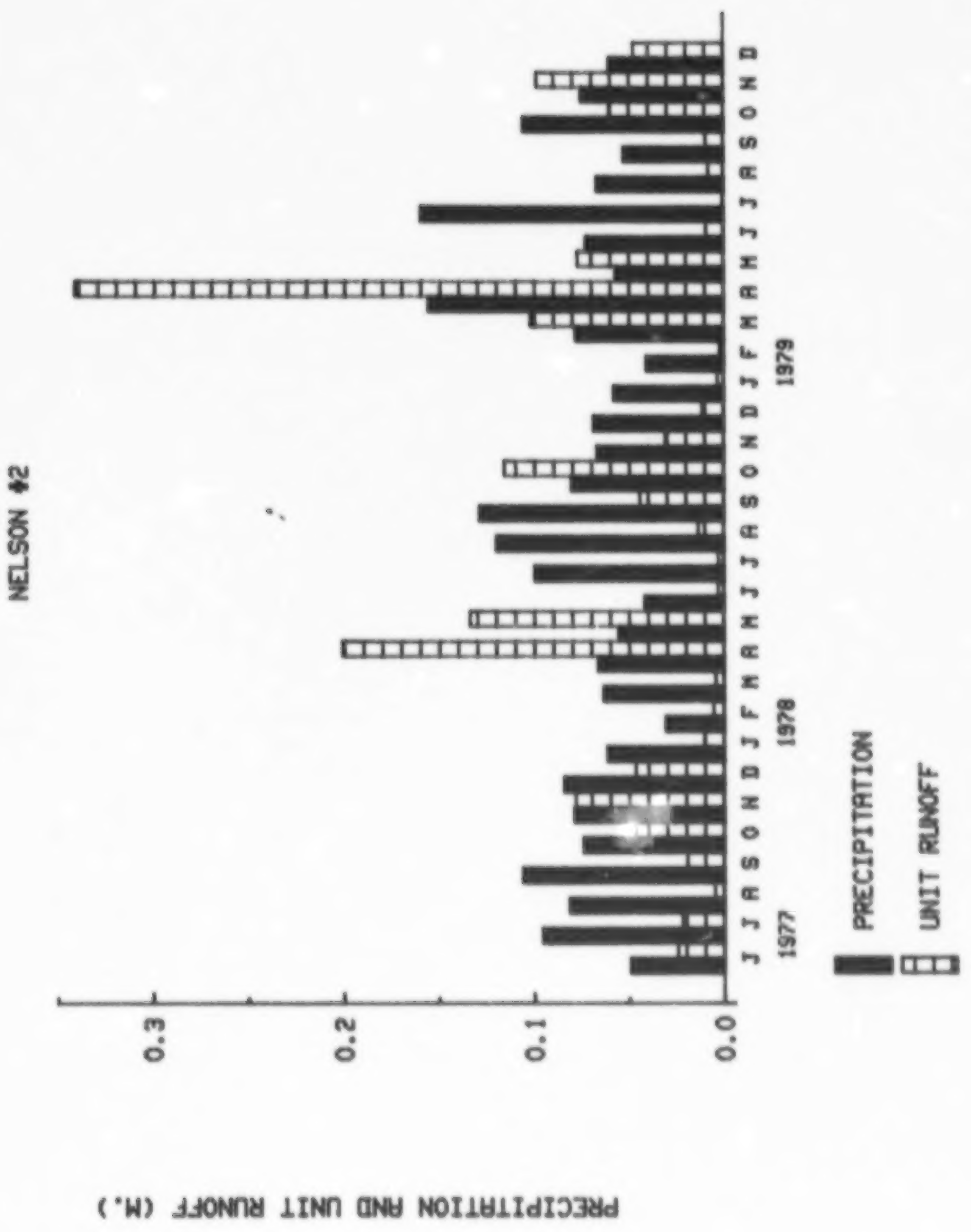
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-7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1977
1978
1979
PRECIPITATION
UNIT RUNOFF

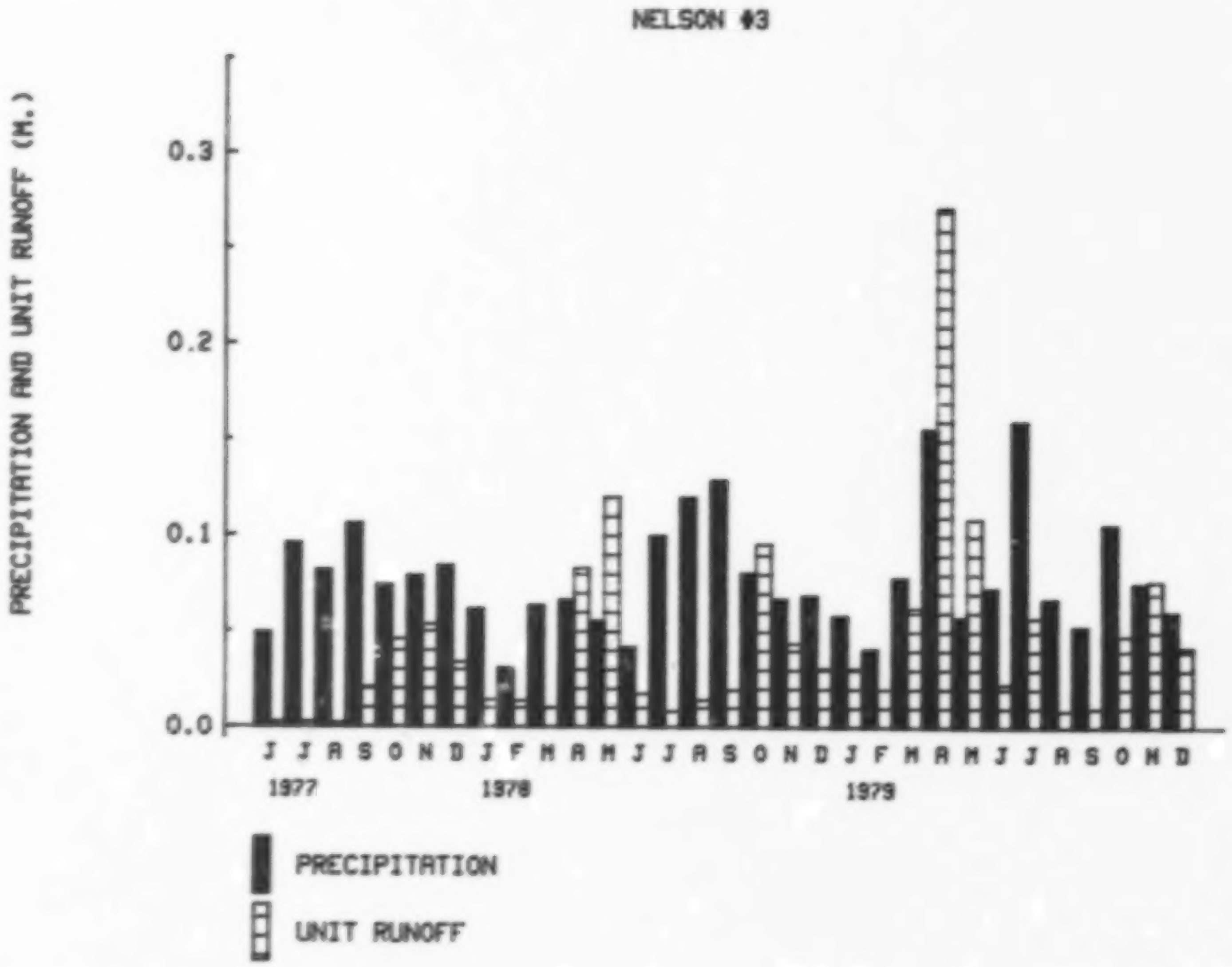
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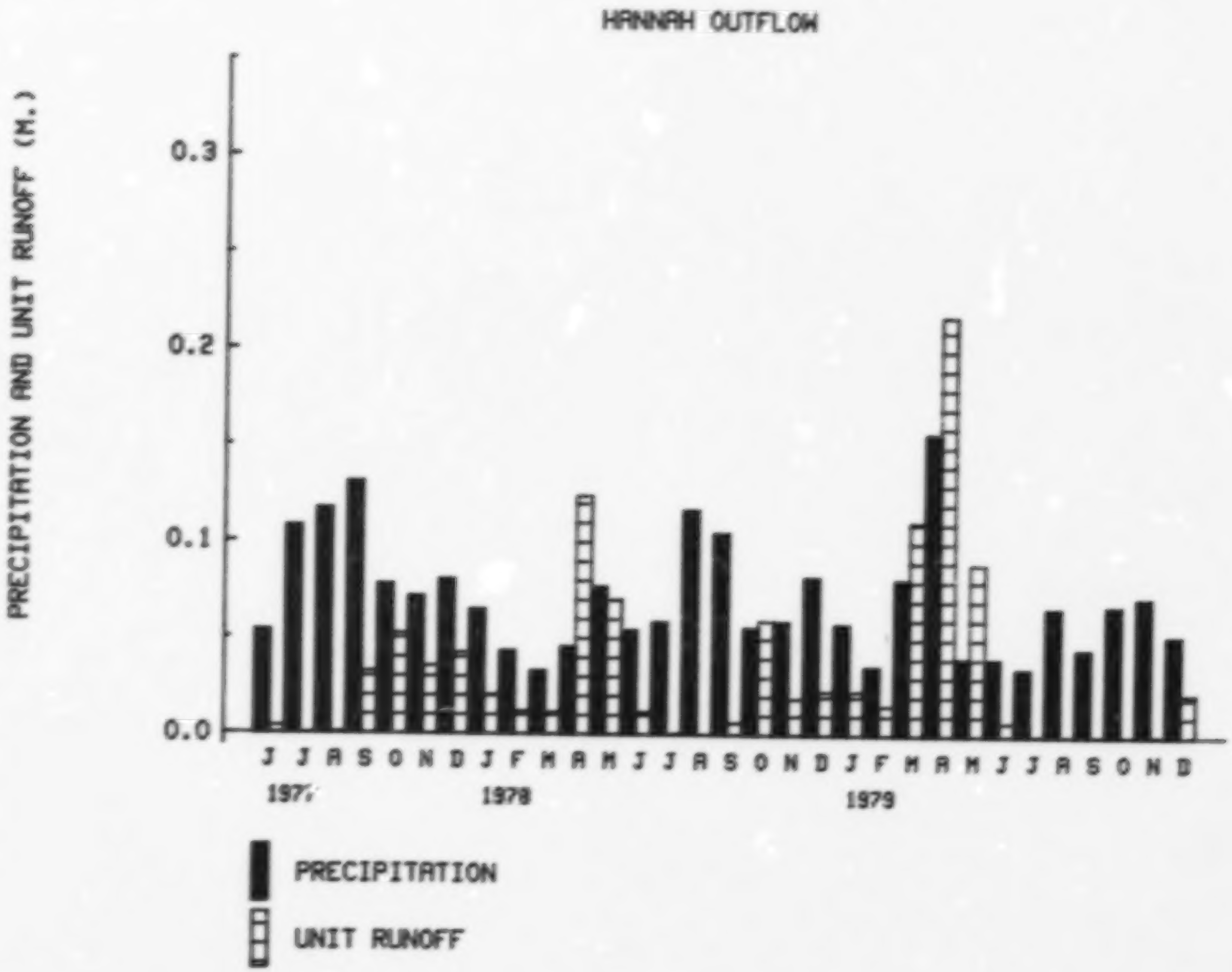
Fig.4-8

Fig.4-9


HANNAH OUTFLOW
PRECIPITATION AND UNIT RUNOFF (M.)
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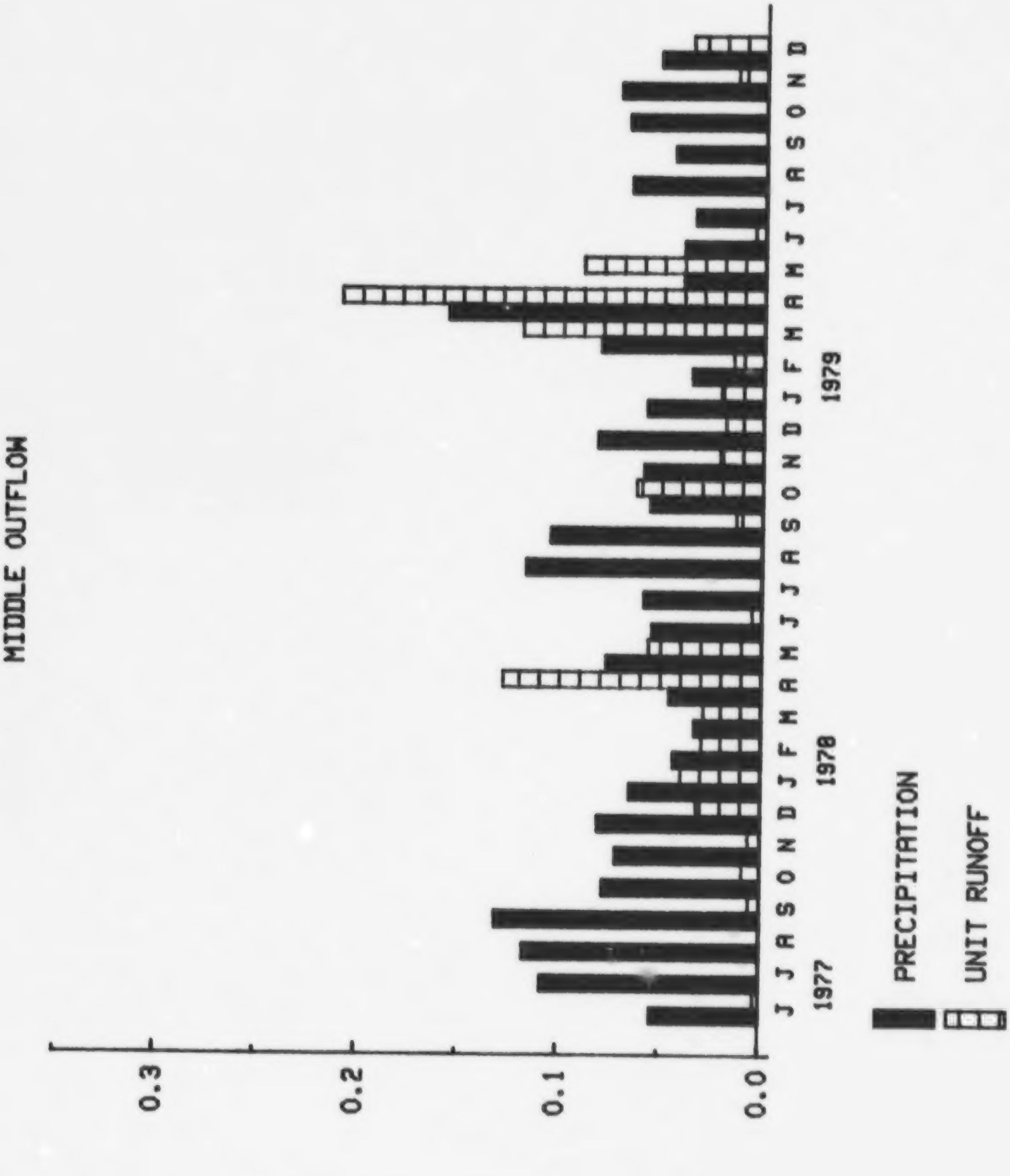
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-10


MIDDLE OUTFLOW
PRECIPITATION AND UNIT RUNOFF (M.)
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0.3
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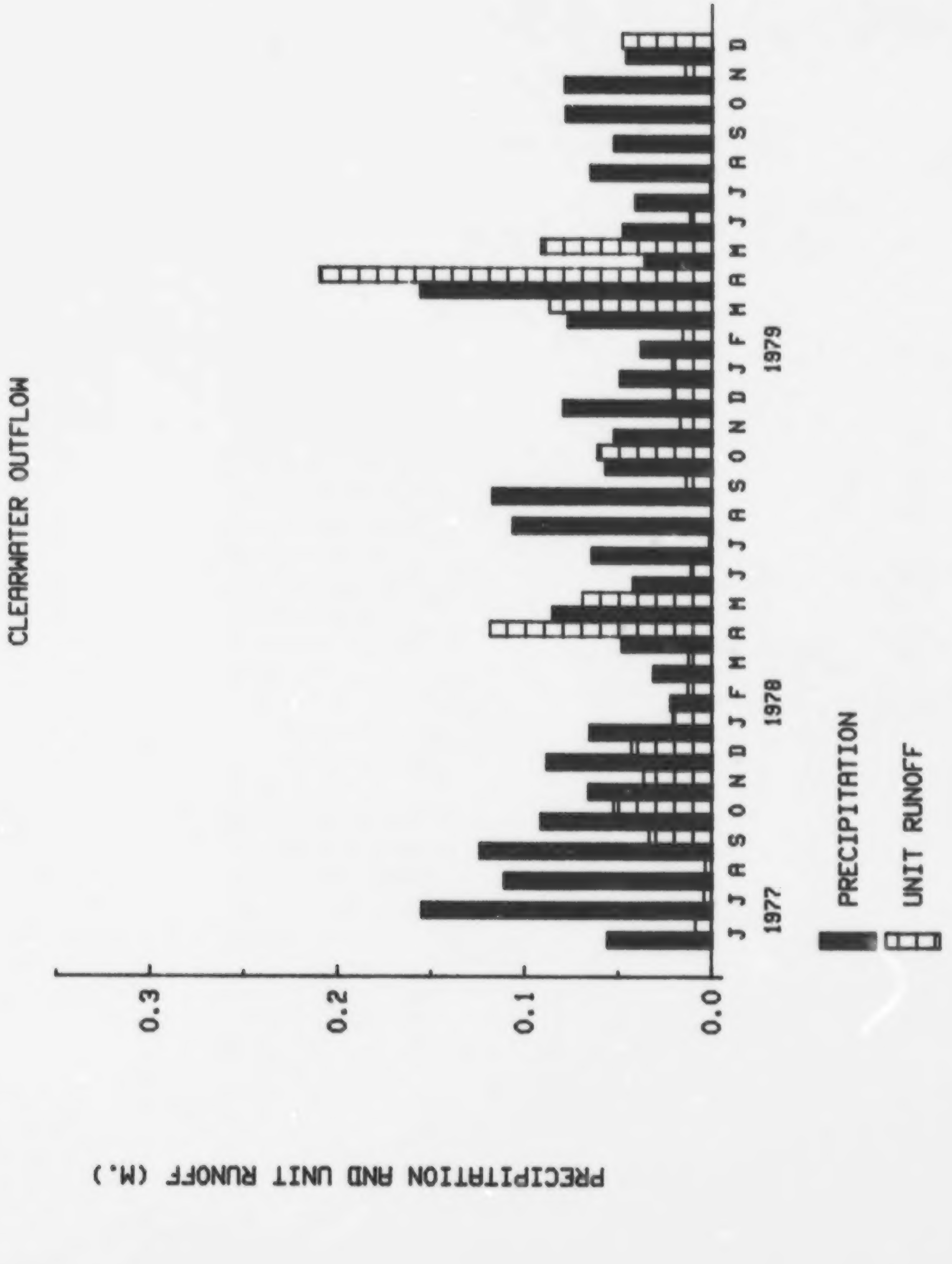
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-11


CLEARWATER OUTFLOW
PRECIPITATION AND UNIT RUNOFF (M.)
0.0
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0.3
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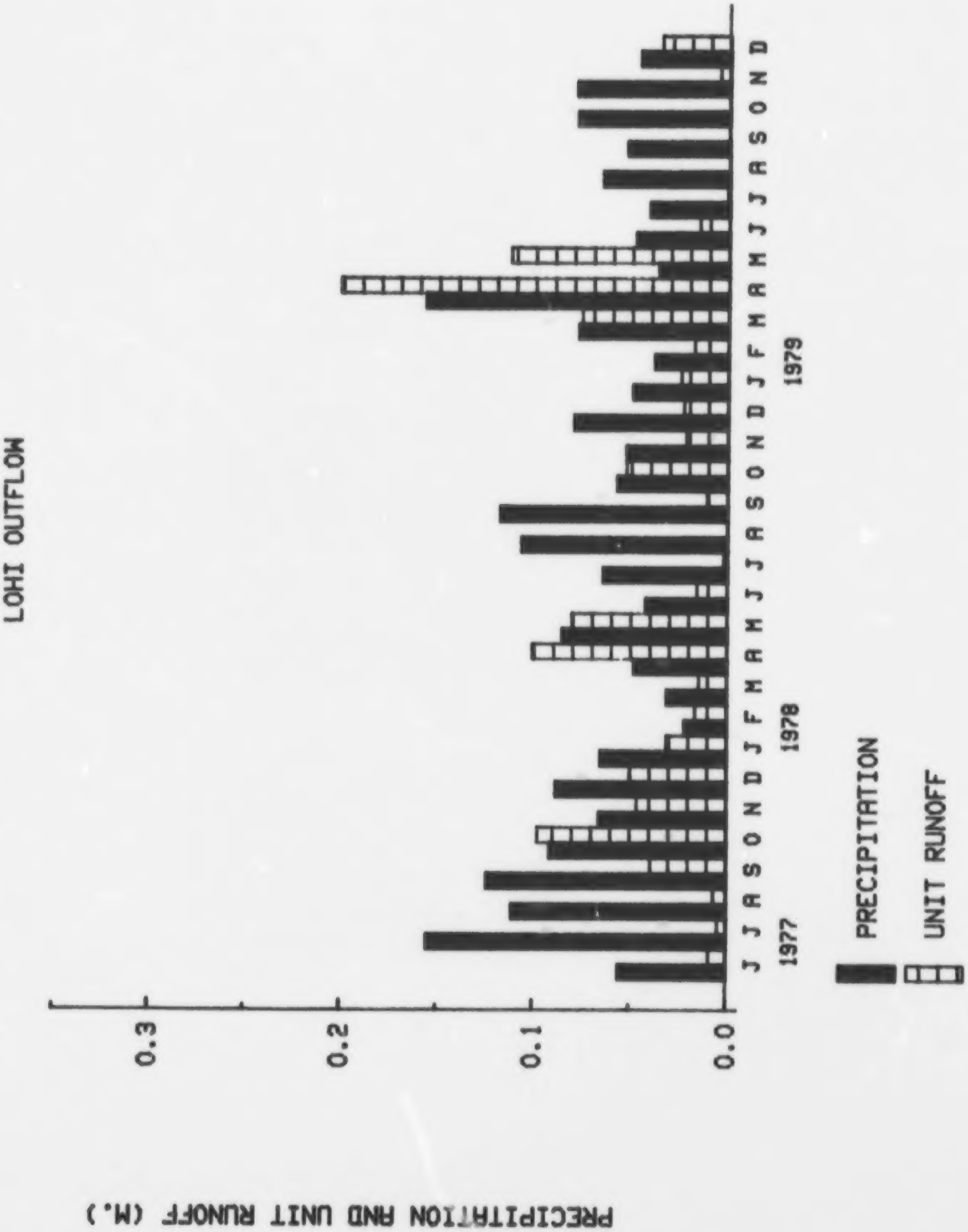
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-12


LOHI OUTFLOW
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0.3
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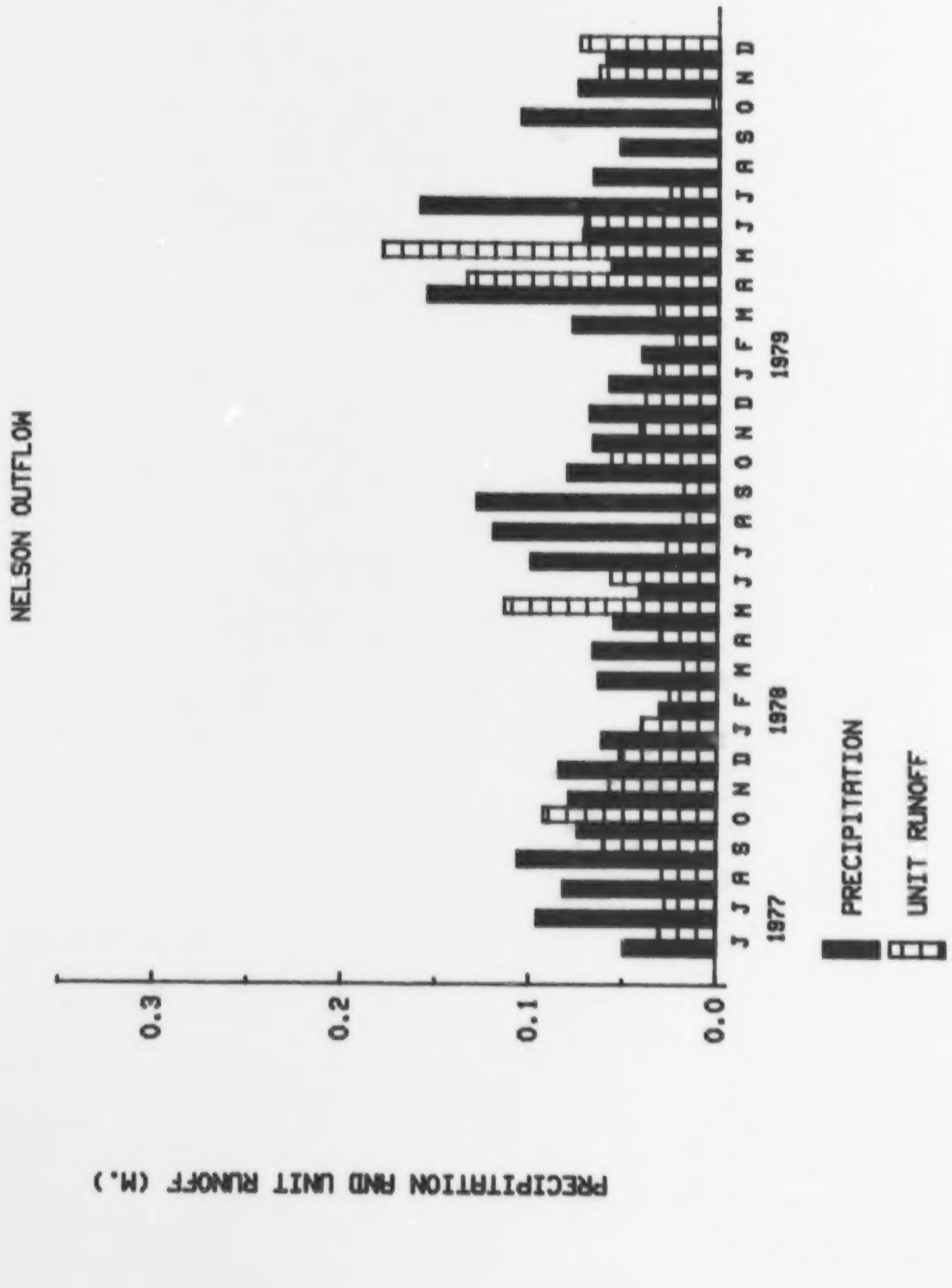
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-13


NELSON OUTFLOW
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0.1
0.2
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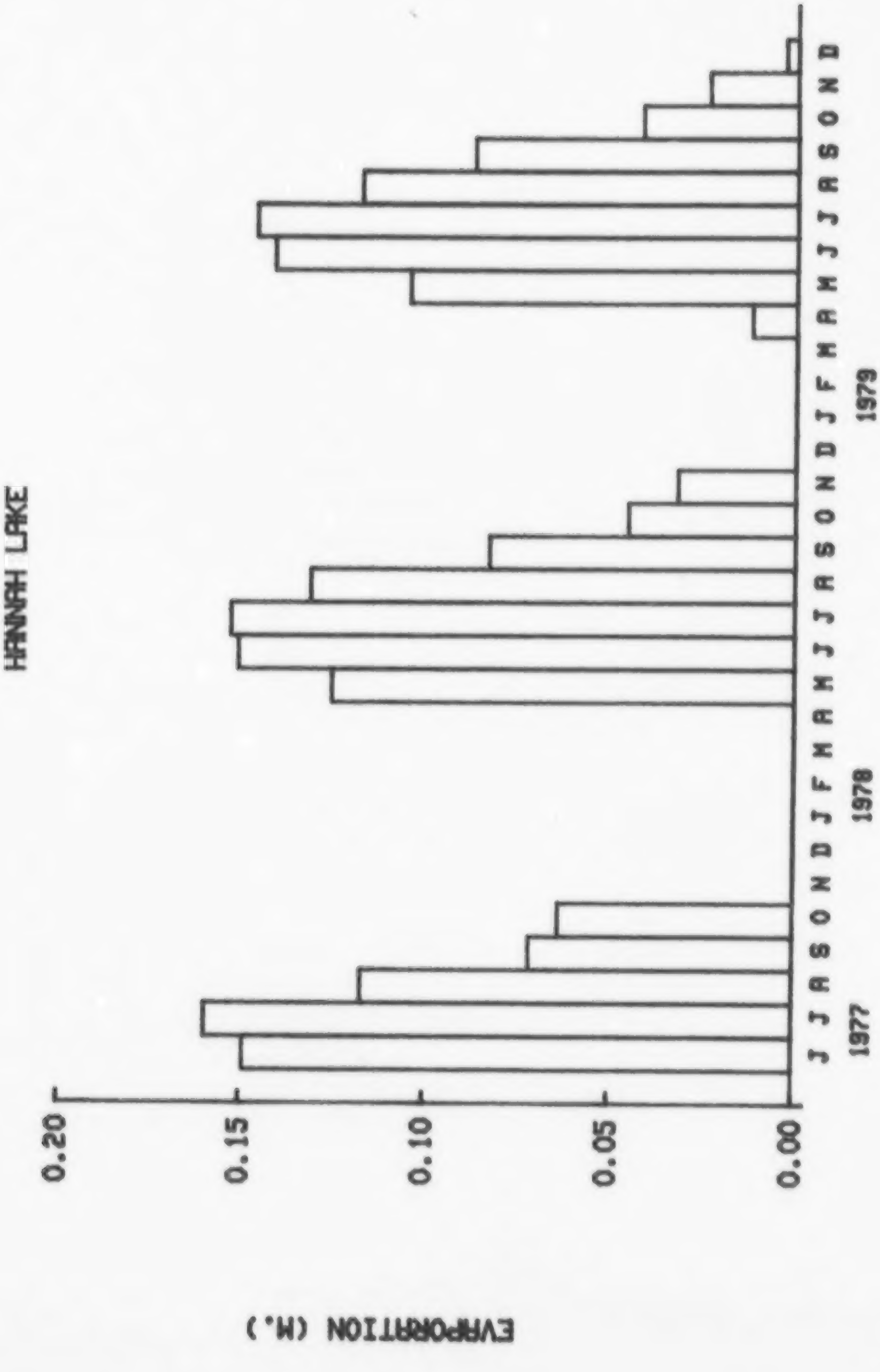
1977
1978
1979
PRECIPITATION
UNIT RUNOFF

Fig.4-14



HANNAH LAKE
EVAPORATION (M.)
0.20
0.15
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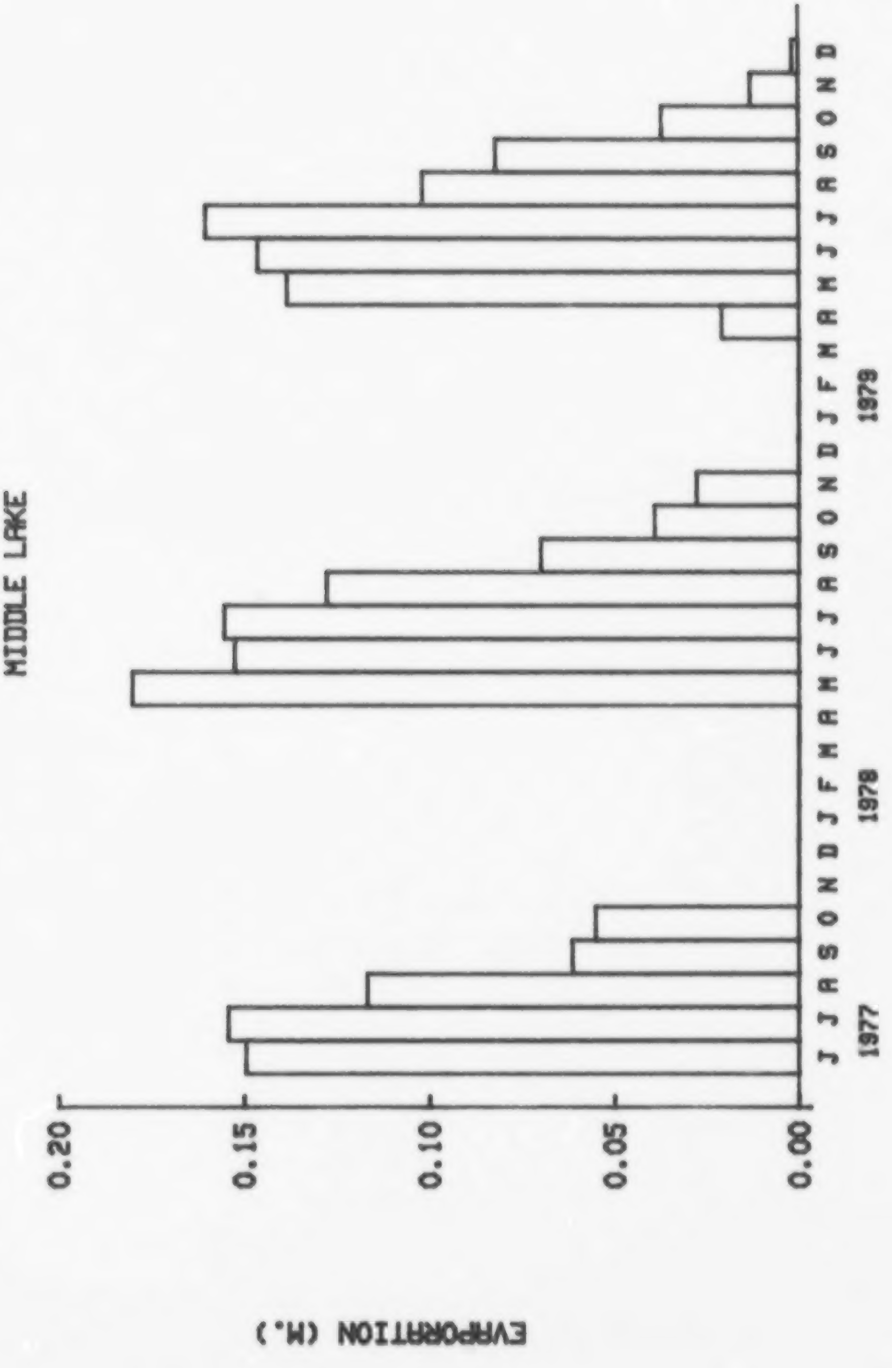
1977
1978
1979

Fig.4-15


MIDDLE LAKE
EVAPORATION (M.)
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0.10
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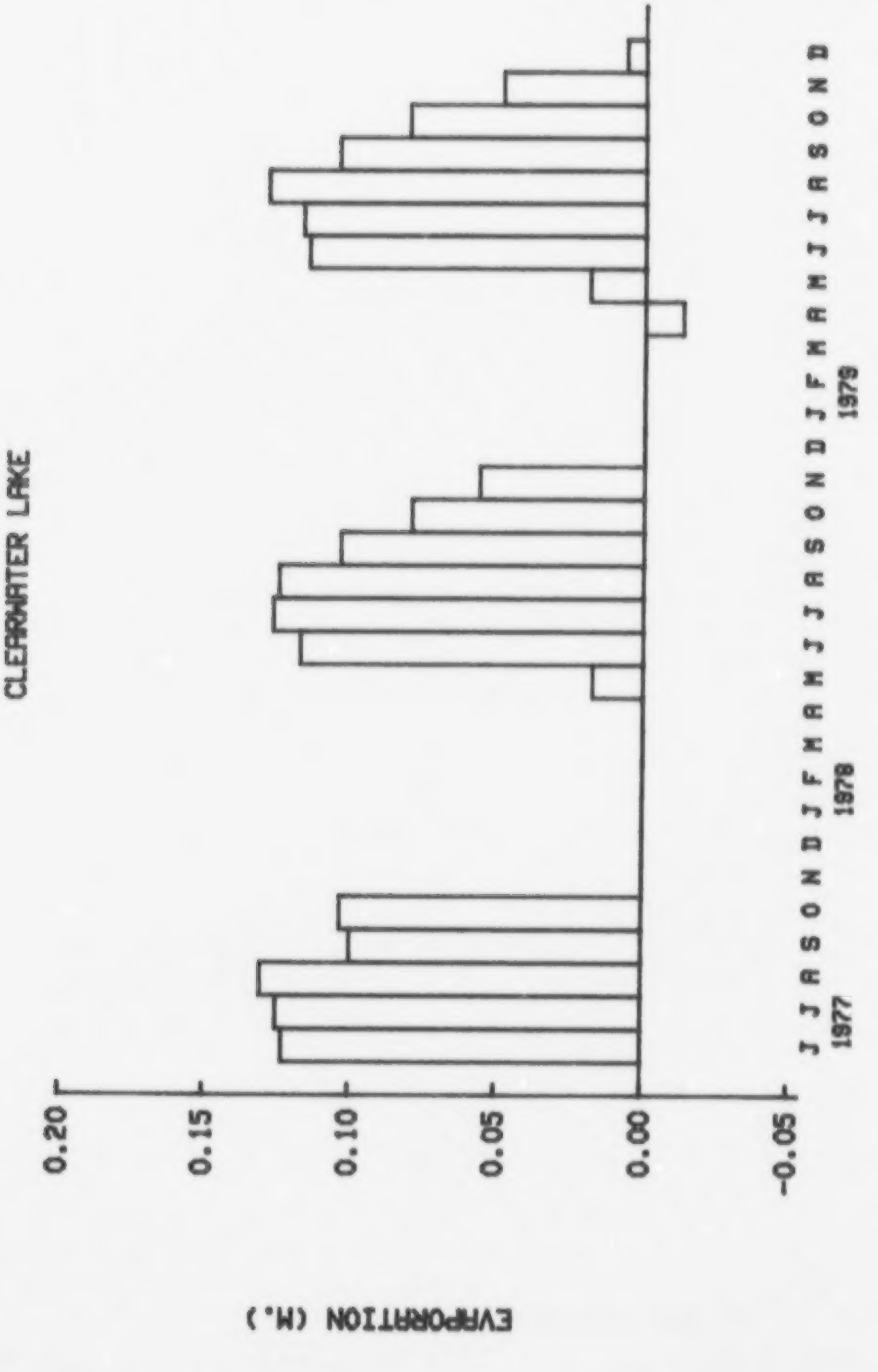
1977
1978
1979

Fig.4-16


CLEARWATER LAKE
EVAPORATION (M.)
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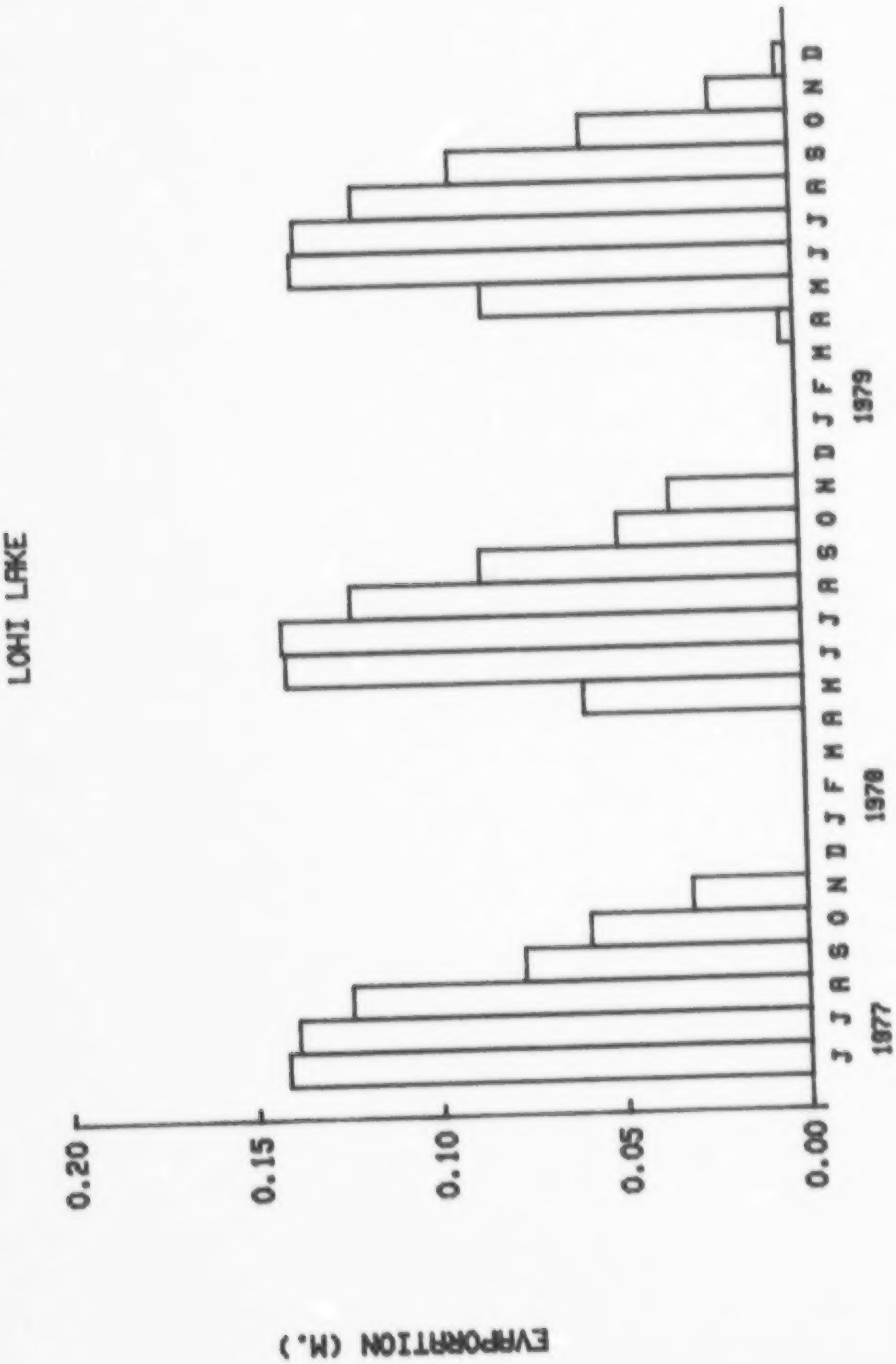
1977
1978
1979

Fig.4-17


LOHI LAKE
EVAPORATION (M.)
0.00
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0.10
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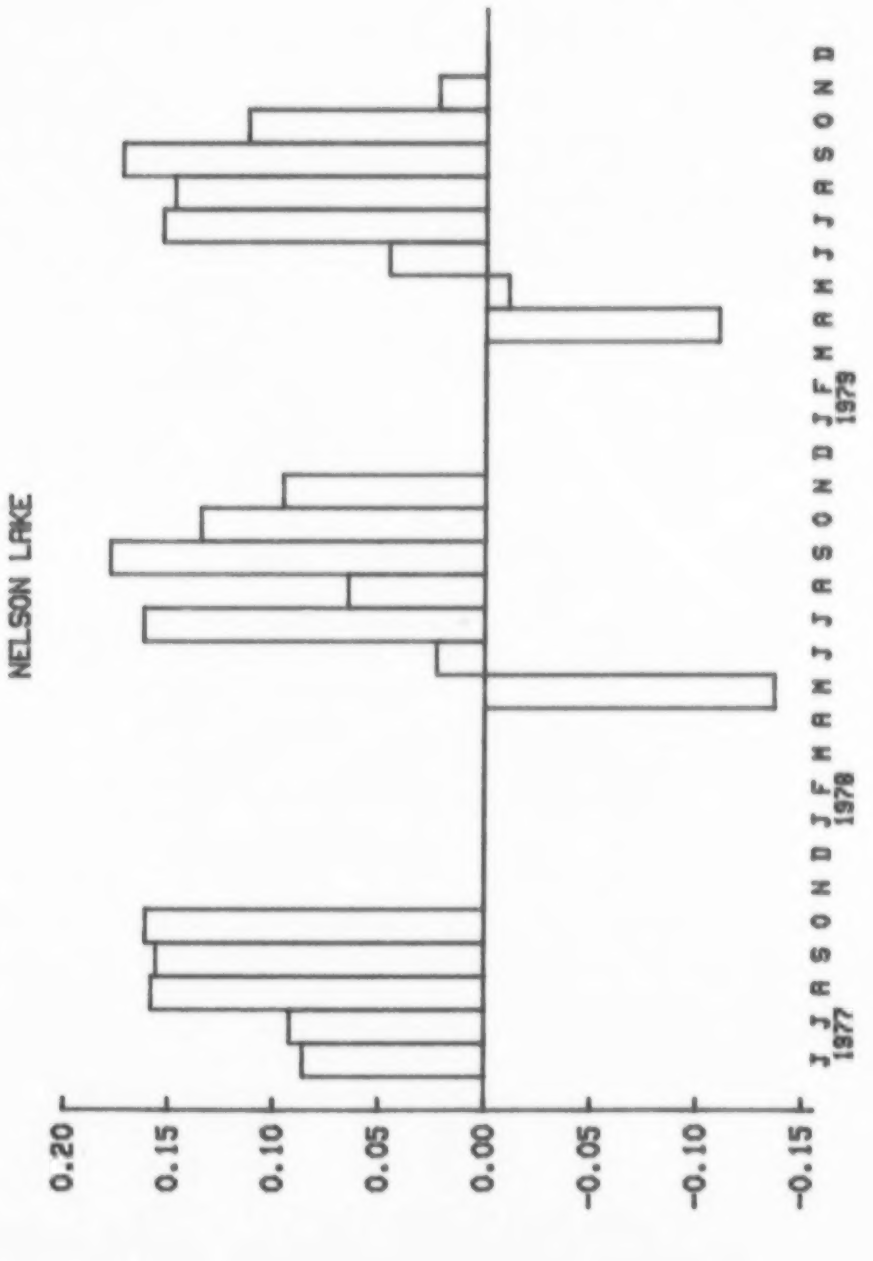
J J A S O N D
1977
J F M A M J J A S O N D
1978
J F M A M J J A S O N D
1979

Fig.4-18


NELSON LAKE
EVAPORATION (M.)
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0.10
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0.00
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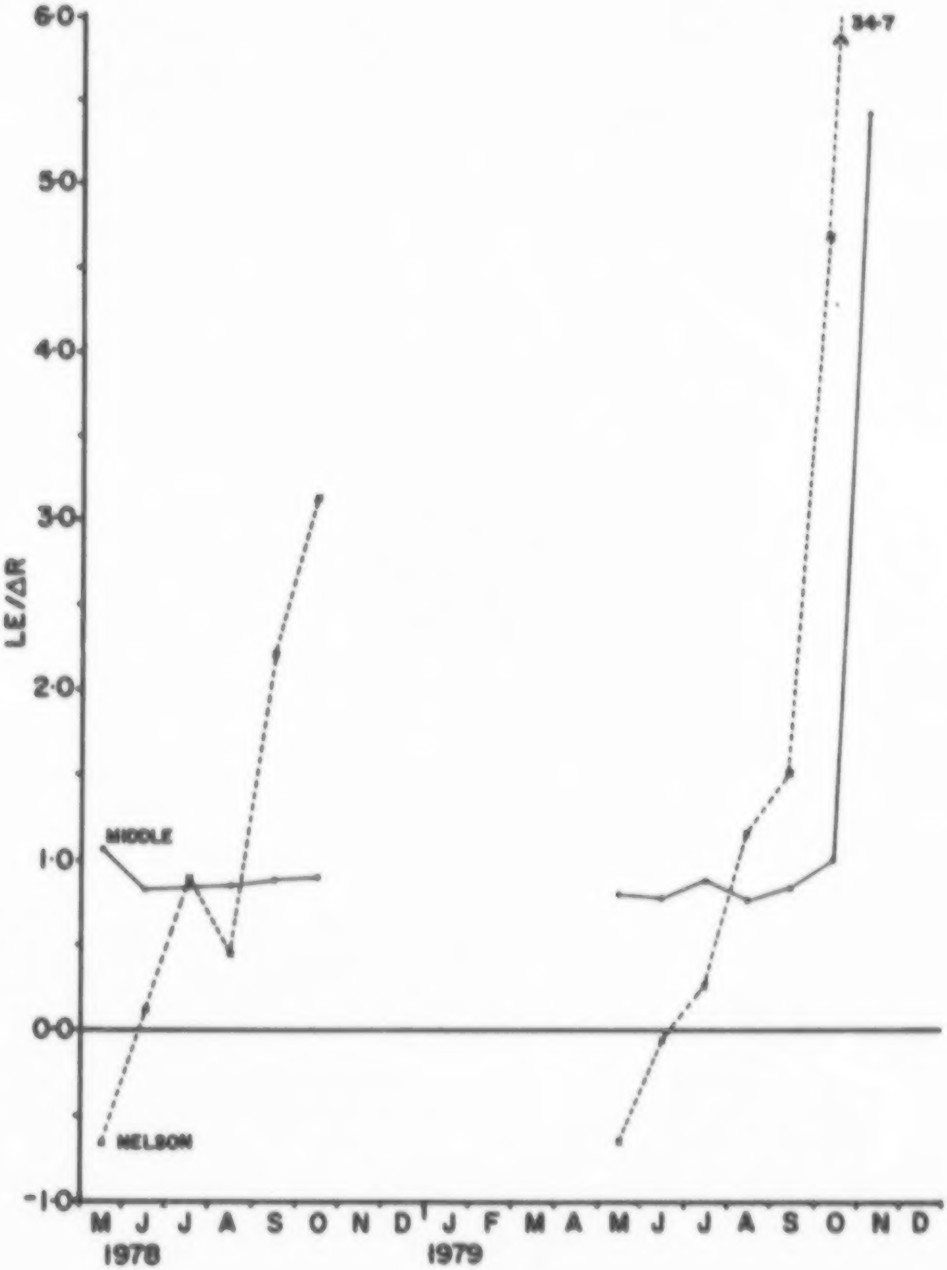
1977
1978
1979

Fig.4-19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LE/ΔR
MIDDLE
NELSON
34·7
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1979

CHAPTER 5

STREAM CHEMISTRY:
GEOCHEMICAL INTERACTIONS OF WATERSHEDS WITH PRECIPITATION NEAR SUDBURY, ONTARIO.

D.S. Jeffries, W.A. Scheider and W.R. Snyder

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A. Introduction and Background

In a geochemical context, information on the chemical composition of streams and the output (export) of material from watersheds is important from 2 points of view. First, streams are the major links between the terrestrial portion of a lake's watershed and the lake. Explanation of observed changes in lake chemistry using mass balance models depends upon accurate measurement or prediction of inputs from the watershed to the lake. The input of material to the lake from the terrestrial watershed and its impact on lake chemistry will be discussed in Chapter 8. Second, stream chemistry is an integrated result of the interaction between precipitation and the bedrock and surficial geology of the watershed. There are, of course, many factors modifying this interaction, including climatic variables (temperature, depth of precipitation), physical characteristics of the watershed (size, slope), vegetation and land use patterns prevalent in the watershed.

In this chapter, we relate stream chemistry and watershed export to the input of material to the watershed from precipitation and to the geochemical processes ongoing in the watershed. Because these interactions may be obscured by the biological activities occurring in lakes (eg. uptake and sedimentation of P, N), we have chosen to deal only with headwater streams. The chemical composition of 11 streams draining into our 5 study lakes was monitored over the period 1976 to 1979. Five of the 11 watersheds were hydrologically gauged (Chapter 4) over the period June 1977 to Dec. 1979. This information was used to predict streamflow for the 6 ungauged watersheds (Appendix 3), and together with measured concentration data, watershed export rates were calculated (Appendix 9).

Water is a major participant in the exogenic geochemical cycle, the slow migration of matter near the earth's surface (Rankama and Sahama 1950). It acts both as a reactant in the chemical transformation of matter and as a conveyor of material in dissolved or suspended form (Stumm and Morgan 1970). The cycle begins with solid crystalline rock and ends with sedimentary rock, usually deposited in a marine environment. The atmosphere provides a transport medium for acids (H_2CO_3, H_2SO_4, NH_4^+, HNO_3, etc.) and oxidants (O_2), the reactants which drive weathering reactions in the watershed.

There are 3 types of mineral weathering reactions: redox reactions, congruent dissolution and incongruent dissolution. At Sudbury, as on a global scale, the incongruent dissolution of silicate minerals is dominant since none of the study watersheds are underlain by carbonate bedrock. As discussed in Appendix 2c, this weathering reaction may be described as follows:

$$\begin{matrix}\text{cation-Al-silicate} \\ +\ \text{acid} + H_2O\end{matrix} \longrightarrow \begin{matrix}\text{acid anion} + H_4SiO_4 \\ +\ \text{cation} + \text{Al-silicate}\end{matrix} \qquad (5\text{-}1)$$

Silicic acid, the cation(s) from the silicate minerals and the anion from the acid are released into solution. The reaction rate is very slow and, in consequence, streams draining silicate terrains are usually very dilute. Weathering of silicate terrains in humid, temperate climates has been extensively studied (Goldich 1938, Feth et al. 1964). Calcium ion and Na^+ are rapidly leached from the parent bedrock during the early stages of weathering. In contrast, Mg^{2+} and Si are generally leached in lesser quantities, but at a relatively constant rate throughout the weathering process.

Potassium is the cation least rapidly leached. A consequence of this weathering sequence is that Ca^{2+} and Na^+ are commonly the most prominent cations in streams. The "Al-silicate" residue remaining after the initial leaching of the cations and Si is a clay mineral. The specific type and composition of the clay is controlled by climatic factors governing the overall weathering rate, primarily the amount of precipitation.

In watersheds not affected by anthropogenic activities, H_2CO_3 is the major acid participating in weathering reactions, with the result that HCO_3^- is the principal anion in waters draining these areas. The H_2CO_3 may be supplied from 2 sources i) CO_2 dissolved in precipitation and ii) CO_2 generated from the oxidation of organic material in the soil and dissolved in the interstitial soil water. However, Likens _et_ _al_. (1977) have shown that, in some small headwater basins, the strong acids (H_2SO_4) dominating precipitation chemistry have influenced the weathering reactions in the basins to the extent that SO_4^{2-} is the major anion in the streams.

B. Stream Chemistry

i. Characterization of Stream Chemistry

The discharge- or volume-weighted mean concentration of each of 20 chemical species are given in Table 5-1 for the 11 monitored streams. Sampling and analytical methods are discussed in Appendix 1. Methods used to calculate mean concentrations are outlined in Appendix 9. The reliability of the data may be assessed by performing a charge balance using the volume-weighted mean concentration data (Table 5-1). For all streams except Nelson 3 and Nelson 6, the sum of the cations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+,

Table 5-1: Volume-weighted mean pH and concentrations (mg L^{-1}) of ions, nutrients, and heavy metals in Sudbury streams from June 1977 to December 1979.

	Stream										
	Clearwater				Middle	Nelson					
Parameter	1	2	3	4	1	1	2	3	4	5	6
pH	4.5	4.4	5.0	4.9	4.6	4.6	4.6	5.4	5.3	5.7	5.4
H^+	0.032	0.040	0.010	0.013	0.025	0.025	0.025	0.004	0.005	0.002	0.004
Ca^{2+}	3.5	12.2	1.1	5.9	6.3	3.6	3.6	4.0	4.7	4.9	4.1
Mg^{2+}	0.9	1.8	0.3	1.2	2.0	0.7	0.6	0.8	1.1	1.2	1.6
Na^+	1.1	4.1	0.5	2.1	1.9	0.9	0.9	1.0	1.1	1.1	1.3
K^+	0.4	0.6	0.2	0.6	0.7	0.3	0.2	0.4	0.5	0.6	0.5
SO_4^{2-}	16.4	17.9	5.0	14.6	27.3	14.1	13.8	14.0	17.7	16.6	14.1
Cl^-	0.5	23.2	0.3	8.2	2.3	0.5	0.4	0.4	0.4	0.4	0.7
HCO_3^-	0	0	0	0.3[1]	0	0	0	3.0[1]	1.1[1]	2.3[1]	1.2[1]
TP	0.009	0.007	0.003	0.011	0.010	0.013	0.008	0.009	0.009	0.010	0.005
NO_3^-	0.026	0.032	0.008	0.043	0.107	0.060	0.009	0.060	0.020	0.092	0.047
NH_4^+	0.022	0.017	0.004	0.088	0.050	0.036	0.016	0.050	0.020	0.087	0.017
TKN	0.231	0.210	0.092	0.340	0.264	0.318	0.206	0.268	0.188	0.322	0.133
Si	3.2	4.1	1.2	3.0	4.3	2.7	3.9	3.5	5.1	3.4	1.3
Fe	0.395	0.232	0.198	0.929	0.296	0.463	0.114	0.233	0.581	0.400	0.184
Mn	0.169	0.222	0.054	0.153	0.186	0.123	0.090	0.041	0.041	0.045	0.048
Al	0.307	0.520	0.124	0.531	0.506	0.275	0.311	0.173	0.174	0.108	0.194
Cu	0.033	0.041	0.010	0.037	0.194	0.008	0.004	0.004	0.006	0.005	0.004
Ni	0.215	0.287	0.061	0.221	0.719	0.029	0.024	0.013	0.011	0.011	0.025
Zn	0.024	0.081	0.015	0.045	0.051	0.016	0.021	0.008	0.007	0.007	0.009
Pb	0.012	0.005	-	-	0.007	0.005	0.007	0.004	0.006	0.008	0.005
Bal[2]	95	96	97	95	95	100	100	88	97	99	80

[1] HCO_3^- as mg L^{-1} $CaCO_3$

[2] Balance = % agreement between total cations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+) and total anions (SO_4^{2-}, Cl^-, NO_3^-, TIA) in μeq L^{-1}.

NH_4^+, in meq L^{-1}) balanced the sum of the anions (SO_4^{2-}, Cl^-, NO_3^-, HCO_3^- to within 5% or less. The difference was 12% for Nelson 3 (anions in excess) and 20% for Nelson 6 (cations in excess). Imprecise measurements of TIA may explain the poorer balance for Nelson 3 (it has the highest alkalinity of all 11 streams), while inaccuracies in the small data set (<20 samples) for Nelson 6 may have resulted in apparent imbalance.

The range in mean concentrations among the 11 streams itself ranged from 3-fold (Pb) to 65-fold (Ni). The mean concentrations of H^+, Ca^{2+}, Cl^-, NO_3^-, NH_4^+, Cu, Ni and Zn all showed a >10 fold range between streams. In the case of nutrients (TP, NO_3^-, NH_4^+, TKN), Cu, Ni and Zn the range in concentration in any single stream over the course of the year was greater (>10 fold variation) than the range between streams. The range in concentration over time for the major ions was generally small, <10 fold except for H^+, Na^+ and Cl^-. The large variation in Na^+ and Cl^- occurred in streams draining watersheds affected by road construction and maintenance, whereas pH depressions during the spring snowmelt and after major precipitation events accounted for the variation in H^+ concentration. Compared to streamflow, which often varied by 2-3 orders of magnitude within a year, the variation in concentration with time was small. However, the range of concentration within a year was large compared with the 2-fold variation reported on average at Hubbard Brook, N.H. (Likens et al. 1977).

The grand arithmetic mean concentrations (geometric mean pH) over 11 streams for each of the 20 chemical species analysed are given in Table 5-2, with data from other granitic terrains in North

Table 5-2: Mean pH and concentration (mg L^{-1}) of all samples (Jan. 1976 - Dec. 1979) for study streams at Sudbury, 66 streams at Muskoka-Haliburton (south-central Ontario, unpub. data), Hubbard Brook (New Hampshire)[1], streams at Sierra Nevada (California)[2], streams of Rawson Lake (N.W. Ontario)[3], and world average river water[4].

Parameter	Sudbury	Muskoka-Haliburton	Hubbard Brook	Sierra Nevada	Rawson Lake	World Average River Water
pH[5]	4.7	5.1	4.9	6.2/6.8	5.5	
Ca^{2+}	5.7	6.6	1.7	3.1/10.4	2.2	15
Mg^{2+}	1.3	1.7	0.4	0.7/1.7	0.8	4.1
Na^{+}	2.1	1.2	0.9	3.0/6.0	1.3	6.3
K^{+}	0.5	0.6	0.2	1.1/1.6	0.4	2.3
SO_4^{2-}	17.2	11.6	6.2	1.0/2.4	3.4	11.2
Cl^{-}	5.7	1.1	0.5	0.5/1.1	0.3	7.8
TIA[6]	<0.0	13.3	1.6	33/89.5	6.2	95.7
TP	0.013	0.032			0.018	
NO_3^{-}	0.038	0.138	0.436	0.005/0.063		0.226
NH_4^{+}	0.059	0.052	0.03			
TKN	0.285	0.467				
Si	3.8	3.2	2.1	7.7/11.5	4.8	6.12
Fe	0.597	0.600		0.03/0.031	0.370	0.67
Mn	0.138	0.068				>0.012
Al	0.325	0.170	0.23	0.03/0.018		
Cu	0.033	0.002				~0.010
Ni	0.168	0.002				~0.010
Zn	0.037	0.011				~0.010
Pb	0.007	0.003				0.001-0.011

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[1] Likens *et al.* (1977), average for 1963-74

[2] Feth *et al.* (1964); values in table for ephemeral and perennial springs, respectively

[3] Schindler *et al.* (1976), data calculated for terrestrial drainage of Rawson Lake. Alkalinity value taken from Armstrong and Schindler (1971), Table 10

[4] Livingstone (1963)

[5] Geometric mean for Sudbury and Muskoka-Haliburton

[6] Alkalinity as mg L^{-1} $CaCO_3$; measured TFA values corrected by 1.6 mg L^{-1}.

America and "world average" river water for comparative purposes. Using these data, the order of importance of ions in streams (on an equivalent basis) for species with concentrations >0.01 meq L^{-1} is given in Table 5-3. If we assume that Al is a trivalent cation, then its concentration often exceeds 0.01 meq L^{-1}. In importance, it would fall between Na^+ and K^+, averaging data for the 11 study streams. However, as shown in Fig. 5-1, some of the Al may be in the 1+ or 2+ valency state over the pH range observed in our streams and, therefore, it may well be of lesser importance.

The order of importance of ions is an indicator of their relative mobility in watersheds and/or the geochemical reactions taking place. It is clear that the bicarbonate-producing reactions which have historically been the primary rock weathering reactions are of little importance in Sudbury watersheds, since HCO_3^- is the least important ion listed. In the Sierra Nevada watersheds (Feth et al. 1964), "natural" weathering reactions predominate and the order of ion importance in streams closely resembles that of "world average" river water, with HCO_3^- dominant. The H^+ concentration of the Sierra Nevada streams is <0.01 meq L^{-1} (pH >5.0).

The order of importance of ions in Sudbury streams is most similar to that observed at Hubbard Brook, N.H. (Likens et al. 1977), with SO_4^{2-} and Ca^{2+} as the 2 dominant ions and H^+ concentration >0.01 meq L^{-1}. There are 2 major differences in the chemistry of streams at Sudbury and Hubbard Brook. The Cl^- concentration is greater in the Sudbury streams because of the input of Cl^- (NaCl and $CaCl_2$) from road maintenance operations. The NO_3^- concentration is lower in the Sudbury streams because of lower input of NO_3^- from precipitation and greater retention of NO_3^- by the watershed. The order of ion dominance in streams

Table 5-3: Order of importance of ions (>0.01 meq L^{-1}) for 11 streams in this study, 66 streams at Muskoka-Haliburton, Rawson Lake (N.W. Ontario), Hubbard Brook (N.H.), Sierra Nevada, world average river water, and Sudbury area bulk precipitation[1].

Sudbury streams	SO_4>Ca>Cl>Mg Na>H>K>
Muskoka-Haliburton	Ca>HCO_3[2]>SO_4>Mg>Na>Cl>K>NO_3 H
Rawson Lake	HCO_3[3]>Ca>SO_4 Mg>Na>K Cl
Hubbard Brook	SO_4>Ca>Na>Mg HCO_3[2] NO_3>Cl H>K
Sierra Nevada -ephemeral	HCO_3[2]>Ca>Na>Mg>K>SO_4>Cl
-perennial	HCO_3[2]>Ca>Na>Mg>SO_4>K>Cl>NO_3
World average river water	HCO_3[2]>Ca>Mg>Na>SO_4>Cl>K>NO_3
Sudbury precipitation	SO_4>H>NO_3>Ca Na NH_4>Cl>Mg>K

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[1] order for streams calculated from data in Table 5-2; for discussion of order in Sudbury bulk precipitation, see Chapter 2

[2] 50 mg L^{-1} Alkalinity (as $CaCO_3$) = 1 meq L^{-1} HCO_3

[3] position of HCO_3 questionable since concentration in Table 5-2 obtained from a different source than the remaining data

entering Rawson Lake in the Experimental Lakes Area (ELA) in N.W. Ontario, perhaps represents an intermediate situation between Sudbury/Hubbard Brook and the Sierra Nevada. The ELA area does receive acidic precipitation (pH ~5.0, Schindler et al. 1976), although the input is not of sufficient consequence to replace the "normal" carbonation reactions. The secondary influence of the strong acid input is evident at ELA in that SO_4^{2-} is more dominant than in the Sierra Nevada streams. The prominence of SO_4^{2-} in the order of ion dominance in Muskoka-Haliburton streams shows that geochemical reactions are proceeding in response to H_2SO_4 inputs (precipatation pH 4.0-4.2, Scheider et al. 1979b)at this location as well. However, carbonation reactions are still important, as HCO_3^- is the second most abundant ion. In a spectrum of geochemical environments, ranging from one end-member in which strong acids drive the weathering reactions to the other end-member in which H_2CO_3 predominates, the 11 Sudbury watersheds and Hubbard Brook more closely approximate the former, the Sierra Nevada watersheds approximate the latter, and the watersheds of the ELA and Muskoka-Haliburton regions are intermediate, with conditions at ELA closer to those at the Sierra Nevada.

It is important to note that we are dealing with low order streams throughout this discussion. Higher order streams at both Sudbury and New Hampshire have chemical properties more similar to "world average" river water, with HCO_3^- the dominant ion (Ontario Ministry of Environment unpubl. results, Johnson et al. 1981). In low order streams in New Hampshire, Johnson et al. (1981) have shown that initial neutralization of acidic precipitation is due to dissolution of metastable Al in the soil. The ultimate reaction neutralizing acidic precipitation is incongruent dissolution of silicate minerals (chemical weathering), which has a slower reaction rate and becomes prevalent in higher order streams.

Holland (1978) has discussed the relative mobility of cations in granitic (felsic) and basaltic (mafic) terrains. Although variable, the order of mobility is generally Ca>Mg>Na>K for both terrain types. This order reflects the degree of disequilibrium between minerals and the environment at the earth's surface. Minerals containing Ca crystallized at the highest temperatures and are thus at the greatest disequilibrium, while K-containing minerals crystallized at the lowest temperatures and weather more slowly. Granitic terrains exhibit a wider (2-50 fold) range of mobility than their basaltic counterparts (<2 fold). Streams draining felsic terrains at Sudbury (Appendix 2C) exhibit an order and range of cation importance, in agreement with Holland's conclusions. The volume-weighted concentrations of cations in streams draining watersheds underlain by mafic bedrock (Nelson 1, 2, and 6) do not differ in range from those draining watersheds underlain by felsic bedrock (Table 5-1), in disagreement with Holland's conclusions. These results suggest that stream chemistry primarily reflects interactions within the surficial deposits, in agreement with the findings of Kaplan et al (1981) who reported that the distribution of water quality in 238 counties in the NE. U.S.A. showed a stronger relationship to soils than to bedrock. The glacially deposited overburden in the Nelson 1, 2 and 6 watersheds may be considered felsic in composition, as opposed to the mafic bedrock. Although the Clearwater 2 watershed is also underlain by mafic bedrock, stream chemistry is affected by a road.

Total P, NO_3^- and TKN concentrations in streams in the Sudbury area are lower (Table 5-2) than those in Muskoka-Haliburton streams, whereas NH_4^+ concentrations are similar and Si concentrations slightly higher. Nitrate concentrations are particularly low, being ~4-fold less in Sudbury streams than in streams in Muskoka-Haliburton and 11-fold less than in Hubbard Brook.

Manganese, Al, Zn and Pb levels in Sudbury streams are 2-3 fold higher than those in Muskoka-Haliburton, while Cu and Ni are 16 and 84-fold higher, respectively. These elevated concentrations reflect the high input of metals via atmospheric deposition (Chapter 2) and/or low average stream pH; pH affects the dissolution and desorption chemistry of metals such that concentrations tend to be higher in streams with a low pH.

Linear regressions were carried out between mean concentrations of chemical species in the 11 Sudbury streams (Table 5-4). Although many significant correlations were observed, correlation analysis must be used with caution when attempting to imply cause and effect relationships. The positive correlation of H^+ with Mn and Al reflects the greater solubility and mobility of the metals in the more acidic watersheds. The negative correlation of H^+ with HCO_3^- implies replacement of carbonic acid weathering (which produces HCO_3^- as a product) by strong acid weathering. The positive correlations among the major cations indicate a common lithologic source and/or road maintenance activities in the watersheds. This latter factor also explains the strong correlation of Cl^- with Ca^{2+} and Na^+. The strong correlation of SO_4^{2-} with Cu and Ni reflects the predominantly atmospheric origin of these materials. No correlations were observed (at $p = 0.01$) for any of the nutrients (TP, TKN, NO_3^-, NH_4^+), although correlations were found at the $p = 0.05$ level of significance. Some correlations among the nutrients are expected

Table 5-4: Significant correlations (p=0.05 and 0.01) between mean parameter concentrations calculated from all samples collected for 11 Sudbury streams, January 1976 to December 1979.

Parameter	Correlating Parameters p=0.01	p=0.05
H^+	Mn, Al, -Alk.	Ni
Ca^{2+}	Mg^{2+}, Na^+, Cl^-	
Mg^{2+}	Ca^{2+}, Na^+, K^+, Ni	Cl^-, SO_4^{2-}, Cu
Na^+	Ca^{2+}, Mg^{2+}, Cl^-, Al	Mn
K^+	Mg^{2+}	SO_4^{2-}, NO_3^-, Cu, Ni
SO_4^{2-}	Cu, Ni	Mg^{2+}, K^+, NO_3^-
Cl^-	Ca^{2+}, Na^+	Mg^{2+}, Mn, Al
HCO_3^-[1]	$-H^+$	-Mn, -Al
TP		TKN, Fe, Zn
NO_3^-		K^+, SO_4^{2-}, Cu
NH_4^+		TKN
TKN		total P, NH_4^+, -Si, Fe
Si		-TKN
Fe	TKN	
Mn	H^+, Al	Na^+, Cl^-, -Alk, Ni
Al	H^+, Na^+, Mn	Cl, -Alk, Ni
Cu	SO_4^{2-}, Ni	Mg^{2+}, K^+, NO_3^-
Ni	Mg^{2+}, SO_4^{2-}, Cu	H^+, K^+, Mn, Al
Zn	-Pb	total P
Pb	-Zn	

[1] HCO_3^- as mg L^{-1} $CaCO_3$, measured TFA values corrected by 1.6 mg L^{-1} for streams with pH >5.0; when pH <5.0, $HCO_3^- = 0$.

(NH_4^+ vs. TKN). The relationship of NO_3^- with SO_4^{2-} and Cu may reflect the relative importance of anthropogenic sources of NO_3^- compared to other nutrients (Chapter 2). The reasons for some correlations (Zn vs. Pb, Fe vs. TKN, Mg vs. Ni) are not obvious.

The weathering regime reflected by stream chemistry may be represented in the form of predominance diagrams. By making calculations based on equilibrium between water concentrations and known weathering end-products, the theoretical boundary conditions may be established towards which natural water systems will proceed. These boundary conditions, which define various stability fields, are given in Fig. 5-2 and have been obtained by plotting the equilibrium constant expression for the appropriate chemical transformation using values from Table 8-4 in Stumm and Morgan (1970). Further discussion on the preparation of predominance diagrams may be found in Garrels and Christ (1965) and Stumm and Morgan (1970).

The chemistry of the 11 SES streams has been plotted on three predominance diagrams in Fig. 5-2. The molar ratios of $[Na^+]/[H^+]$, $[Ca^{2+}]/[H^+]^2$, and $[K^+]/[H^+]$ are plotted as a function of [Si] (or $[H_4SiO_4]$). All of the points fall in the stability field of kaolinite, implying that the cation ratios in the streams indicate that kaolinite is the stable, final end-product of weathering at Sudbury. This is typical of most surface waters in temperate climates (see additional points plotted on diagrams). Hence, in terms of an overall weathering regime, Sudbury stream waters are not unusual, although the low pH of some of them results in lower ordinate values than any of the other waters in Table 5-2. Once again, it should be noted that use of predominance diagrams implies assumption of equilibrium conditions.

ii. Modelling Stream Chemistry

To investigate the differences observed in stream chemistry between the headwater basins, we used a step-wise multi-linear regression technique with geological descriptions of the watersheds as independent variables (Appendix 2).

The independent variables that we used are summarized in Table 5-5 and were as follows:

a.) Bedrock geology. The bedrock geology of the watersheds was divided into two categories for input into the regression:

1) % of surface area of watershed underlain by felsic bedrock (B1), which includes granophyre, quartzite and gneiss (migmatite and granitic inclusions)

2) % of surface area of watershed underlain by mafic bedrock (B2) which includes volcanic tuff and breccia and gabbro (metagabbro).

b.) Surficial geology. The surficial geology of the watersheds was simplified to 4 categories for the regression analysis:

1) % of surface area of watershed underlain by deposits which allow a major interaction with precipitation falling on the watershed (S1). These deposits were usually >1 m in depth and include minor till, outwash and sand.

2) % of surface area of watershed underlain by deposits which allow a minor interaction with precipitation falling on the basin (S2). These deposits are usually <1m in depth and include thin till and boulder outwash.

3) % of surface area of watershed underlain by deposits allowing only minimal interaction with preciptiation (S3). This includes exposed bedrock.

4) % of surface area of watershed underlain by deposits which are the site of organic accumulation (S4). This includes

Table 5-5: Area ($m^2 \times 10^4$), bedrock geology, surficial geology, and road factor [1], for 11 study watersheds.

		Bedrock Geology		Surficial Geology				
Watershed	Area ($m^2 \times 10^4$)	% Felsic(B1)	% Mafic(B2)	% >1m thick(S1)	% <1m thick(S2)	% Exposed Bedrock(S3)	% area of organic accumulation(S4)	Road Factor[1]
Clearwater 1	90.5	100	0	0	1	87	12	0
Clearwater 2	26.8	35	65	0	0	90	10	10.8
Clearwater 3	22.2	100	0	0	27	68	5	0
Clearwater 4	66.5	76	24	0	0	83	17	13.1
Middle 1	3.6	100	0	0	0	98	2	0
Nelson 1	105	11	89	34	48	1	17	0
Nelson 2	44.3	3	97	35	58	5	3	0
Nelson 3	81.7	100	0	74	17	2	7	0
Nelson 4	58.4	100	0	75	24	0	1	0
Nelson 5	89.2	100	0	83	6	1	10	0
Nelson 6	10.1	0	100	15	78	7	0	0

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[1] Road factor = length of road treated for ice and/or dust control/watershed area.

peat (all kinds) and ponds.

c. A road factor (R) which is defined as the length of road in the watershed which is treated with $CaCl_2$ or NaCl (for the purposes of dust or ice control) divided by the watershed area.

The dependent variable was the arithmetic mean concentration of each chemical species (in mg L^{-1} or the geometric mean in case of pH) for each of the 11 headwater streams using all samples collected over the duration of the study. The regression technique was not applied to the annual export data since only 5 of the 11 headwater basins were hydrologically calibrated and this small number of basins is insufficient for meaningful statistical analysis.

A stepwise regression program (adapted from Jennrich 1977) was used in the analysis. The program initially evaluates the correlation matrix between the dependent and independent variables and selects the variables with the highest correlation coefficient. The variable which increases the significance of the regression by the greatest degree is then added and this step iterated until either no variables remain, no variables can be added due to degree of freedom restrictions or no variable substantially improves the significance of the regression (F-to-enter >4, Jennrich 1977). Provision is also made within each iteration to delete variables if their contribution to the significance of the regression drops below a specified value (4). Matrix stability was tested using a tolerance of 0.01 (Jennrich 1977). Once the computation of the step-wise procedure was complete, the significance of the regression for each step was determined and the equation of the greatest significance ($p < 0.10$) with the least number of independent variables was selected. In a few instances, no significant regression was found.

Regression equations developed for our data set by this procedure have several limitations. These include the following:

a) The correlation of two variables does not necessarily imply that a cause-effect relationship exists. The interpretation of the regression analysis results in this way should be viewed with caution.

b) The independent variables are in some cases themselves correlated (e.g.% felsic vs % mafic bedrock).

c) The number of watersheds used to develop the regression equations is small (11) and the equations have not been applied to an independent set of data to test their predictive ability;

d) The regression equations developed should not be used to make predictions for watersheds which lie outside the study area (~50 km radius from Sudbury), or for watersheds with bedrock geology, surficial geology or road factors outside the range of our data. Disregarding this restriction may lead to the prediction of unrealistically high or low (negative) concentrations. It is possible to predict small negative values even within the range of our data due to the variance in the data. In these cases, the negative values denote near-zero concentrations.

The results of the step-wise regression technique with mean concentrations as the dependent variables are given in Table 5-6. Bicarbonate , total P, NO_3^-, NH_4^+, Zn and Pb were not significantly correlated to any geological or physical characteristics of the watershed. The mean concentration is therefore

Table 5-6 : Results of stepwise procedure to determine the multi-linear relationship between parameter concentration (dependent variable, mg L^{-1}) and watershed descriptors (independent variables, see Table 7-16) for 11 study streams. Multilinear equation, r^2, and significance of the regression are presented. Note that equation for HCO_3^- as mg L^{-1} $CaCO_3$ only applies to streams with pH >5.0; for streams with pH <5.0, $HCO_3^- = 0$.

Parameter Concentration (mg L^{-1})	Equation[1]	r^2	Significance (P)
H^+	0.0261 - 0.00028(S1)	0.58	0.010
Ca^{2+}	4.46 + 0.423(R)	0.55	0.010
Mg^{2+}	1.54 - 0.013(S2)	0.43	0.050
Na^+	1.29 + 0.195(R)	0.70	0.005
K^+	0.552 - 0.003(S2)	0.31	0.100
SO_4^{2-}	15.1 + 0.057(S3)	0.32	0.100
Cl	0.995 + 1.42(R)	0.71	0.005
HCO_3^- [2]	no sig. equation, when pH >5.0, mean = 1.76	–	–
TP	no sig. equation; mean = 0.013	–	–
NO_3^-	no sig. equation; mean = 0.059	–	–
NH_4^+	no sig. equation; mean = 0.038	–	–
TKN	0.320 - 0.002(S2)	0.46	0.025
Si	4.85 - 0.144(S4) + 0.083(R)	0.84	0.001
Fe	no sig. equation; mean = 0.597	–	–
Mn	0.082 + 0.002(S3) - 0.0005(B1)	0.88	0.001
Al	0.192 + 0.003(S3)	0.74	0.001
Cu	-0.0002 + 0.001(S3)	0.45	0.025
Ni	-0.005 + 0.004(S3)	0.66	0.005
Zn	no sig. equation; mean = 0.037	–	–
Pb	no sig. equation; mean = 0.007	–	–

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[1] Independent variables are as follows (see text) and Table 5-5):

B1 = felsic bedrock
B2 = mafic bedrock
S1 = thick surficial deposits
S2 = thin surficial deposits
S3 = exposed bedrock
S4 = organic accumulation
R = length of treated road

[2] HCO_3^- as mg L^{-1} $CaCO_3$, measured TFA values corrected by 1.6 mg L^{-1} for streams with pH >5.0; when pH <5.0, $HCO_3^- = 0$.

provided as the best value for estimating concentrations in other streams.

Calcium, Na^+ and Cl^- were related ($p < 0.01$) to the presence of treated roads within the watershed. Of the 11 streams considered, only Clearwater 2 and 4 had roads treated with NaCl or $CaCl_2$ and their influence on the chemistry of the stream is clear in Table 5-1. If the Clearwater 2 and 4 basins are excluded from the step-wise regression procedure, Ca^{2+} is not significantly correlated with any geological or physical characteristics of the watershed. However, Na^+ and Cl^- concentrations both correlate with the percent of exposed bedrock ($p = 0.01$) which may simply reflect the fact that those watersheds with the greater percent exposed bedrock are also those closest to urban Sudbury where the influence of road salting would be greatest.

The road factor was also included as a second independent variable in the regression with Si. The extent of the watershed covered by areas where organic accumulation is occurring (peat bogs, ponds, etc.) was selected first. The concentration of Si may be inversely related to the area of organic accumulation for two reasons. First, these areas physically restrict the interaction of precipitation with the lithologic materials and thus reduce weathering. Secondly, the areas of organic accumulation may utilize a portion of the Si as the drainage waters pass through these biologically active areas. A positive relationship between Si concentration and the road factor presumably arises from the effect of road sanding in the winter and, for gravel roads, the near constant mechanical weathering due to traffic. The fresh mineral surfaces are more readily leached of Si than the undisturbed rocks in other watersheds.

Hydrogen ion concentration was related to the extent of thick surficial deposits. As the % of the basin covered by these deposits increased, the mean H^+ concentration in the stream decreased. This may occur because more of the incoming H^+ is consumed in weathering reactions in the deeper deposits.

The % of the watershed area covered by thin surficial deposits was inversely correlated with the mean Mg^{2+}, K^+, and TKN concentrations in the streams. No obvious explanation for these relationships is apparent.

Finally, SO_4^{2-}, Mn, Al, Cu and Ni concentrations were all positively correlated with the extent of exposed bedrock in the watershed. The major source of SO_4^{2-}, Cu and Ni in the streams is atmospheric deposition. Areas of exposed bedrock in the watershed probably retain less of the input than do areas of unconsolidated surficial materials because bedrock has a lower capacity for ion exchange mechanisms and possibly because biological mechanisms play a smaller role. However, it should also be noted that the watersheds with the greatest extent of exposed bedrock are also those closest to the source of the emissions and receive greater deposition of Cu, Ni and SO_4^{2-} (see Chapter 2).

In contrast, the atmospheric deposition of Mn and Al is not as important as the input from weathering reactions in the watershed. The extent of exposed bedrock in the watershed shows a positive correlation ($r = 0.72$) to H^+ concentration in the stream. The higher H^+ concentration in the water draining the basin may result in increased leaching or cation exchange of Al and Mn from lithologic materials. The negative correlation of felsic bedrock with Mn concentration in this regression may simply reflect the fact that this rock type (and the associated soils) probably contains less leachable Mn than its mafic counterpart.

C. Gross Export from Watershed

Annual gross export from the watershed is defined as the total output of dissolved or suspended material via streamflow from the watershed, expressed per unit area of watershed. Tables 5-7 and 5-8 give gross export values for the 11 Sudbury watersheds for the periods June 1977 - May 1978 and June 1978 - May 1979, respectively. The range (calculated here as maximum/minimum) in export within a given year between the 11 streams itself showed great variability for the 19 chemical species analysed. In the period June 1977 - May 1978, Ni showed the greatest range (77.5-fold) in export and Si the least (1.9-fold). H^+, Cl^-, NO_3^-, Cu, Ni and Zn all had >10 fold range and the mean range was 18.6-fold. In the period June 1978 - May 1979, Cl^- exhibited the maximum range (53.8-fold) and SO_4^{2-} showed the least range (1.8-fold). H^+, Cl^-, Cu and Ni had >10-fold variation between streams and the mean range was 12.6-fold. The variability in runoff between streams was much smaller (range of 1.2) than the variability in material export. The variability between watershed exports can be largely explained on the basis of the bedrock and surficial geology of the watershed and the existence of roads in the watershed as discussed in the stream chemistry section.

The mean range in material export between the 2 study years (June 1977 - May 1978 vs. June 1978 - May 1979) was 2.1-fold, with a maximum range of 3.3-fold (Cl^-) and a minimum range of 1.4-fold (Na^+). This range was almost invariably less than the range in export between the 11 watersheds in a given year. In part, this is due to the fact that only 2 years of data are available. Schindler et al. (1976), reporting on 4 years of export data for watersheds of Rawson Lake, N.W. Ontario, found between-year variation in export to

Table 5-7: Gross export (mg m^{-2} yr^{-1}) from Sudbury watersheds for the period June 1977 - May 1978 inclusive.

	Clearwater				Nelson						Middle
	1	2	3	4	1	2	3	4	5	6	1
H^+	20.5	26.5	18.1	6.97	14.3	16.6	1.54	2.88	0.808	1.85	16.7
Ca^{2+}	1820	6840	1740	3430	2050	2310	1620	2490	2800	2150	3660
Mg^{2+}	472	1050	436	718	436	440	363	635	756	1700	1180
Na^+	615	2580	854	1160	523	619	443	641	622	639	1110
K^+	241	378	251	334	203	130	155	237	310	272	418
SO_4^{2-}	8450	9550	8240	8310	8020	8850	5700	9440	9430	7580	15800
Cl^-	346	13700	668	4480	271	245	189	253	259	222	1420
HCO_3^-	45.7[1]	0.0	0.0	151[1]	18.6[1]	0.0	44.3[1]	58.1[1]	1790[1]	1230[1]	0.0
TP	6.09	4.53	6.77	7.58	6.89	4.75	3.20	4.76	6.13	3.13	5.61
NO_3^-	18.4	32.7	18.5	26.2	31.8	4.72	17.8	11.2	64.2	27.4	72.1
NH_4^+	12.4	12.5	8.93	62.5	14.3	12.3	12.9	10.0	77.1	8.75	28.8
TKN	144	128	177	205	163	127	107	43.9	196	66.4	156
Si	1740	2250	2110	1680	1410	2300	1380	2680	1750	2250	2280
Fe	296	124	375	703	216	46.0	79.3	284	251	102	173
Al	154	334	226	326	142	203	66.6	99.7	53.0	94.0	275
Mn	90.0	126	90.9	87.0	72.6	53.7	16.3	21.2	17.4	24.2	104
Cu	20.9	26.3	21.0	22.2	4.22	2.90	1.83	4.15	2.89	2.36	115
Ni	113	175	98.8	126	16.7	15.3	5.21	6.81	6.22	12.0	404
Zn	11.7	48.2	29.2	25.4	9.21	13.4	2.95	3.79	3.44	4.26	24.2

[1] HCO_3^- as mg m^{-2} yr^{-1} $CaCO_3$

Table 5-8: Gross export (mg m^{-2} yr^{-1}) from Sudbury watersheds for the period June 1978 - May 1979 inclusive.

	Clearwater				Nelson						Middle
	1	2	3	4	1	2	3	4	5	6	1
H^+	18.5	18.5	16.5	8.3	18.7	16.6	3.67	4.31	1.64	3.72	11.4
Ca^{2+}	2150	6110	1900	3510	2520	2600	2600	3600	3720	3140	3440
Mg^{2+}	535	909	438	700	480	432	534	845	872	598	1050
Na^+	696	2190	813	1200	612	643	679	835	874	795	1020
K^+	306	411	273	337	263	181	303	424	435	381	391
$SO_4{}^{2-}$	10100	9820	9020	8520	9940	9870	9270	13500	12700	10800	15000
Cl^-	300	11300	455	5110	357	210	289	315	321	736	1130
HCO_3^-	53.3[1]	0.0	0.0	78.8[1]	39.8[1]	10.8[1]	744[1]	763[1]	1640[1]	909[1]	0.0
TP	5.90	4.31	3.88	4.80	8.85	4.27	6.25	6.76	6.82	4.01	5.45
NO_3^-	16.3	10.5	9.60	23.6	45.2	6.80	34.8	14.3	60.3	33.2	43.4
NH_4^+	14.7	7.95	6.32	36.5	28.7	8.68	28.4	15.3	46.4	14.8	25.5
TKN	157	132	137	181	236	141	180	153	233	106	138
Si	2230	2460	2050	1730	2110	2760	2680	3830	2970	3330	2550
Fe	239	172	281	381	320	59.2	175	396	271	136	152
Al	204	274	199	294	214	214	138	128	93.2	165	297
Mn	106	122	95.9	90.9	85.9	66.3	31.2	29.8	25.5	40.2	106
Cu	20.2	22.8	11.7	20.5	5.76	2.76	2.98	4.19	3.08	2.35	101
Ni	135	145	113	132	20.4	17.8	9.51	7.78	8.27	21.0	406
Zn	16.3	39.3	21.4	26.1	11.5	16.4	6.36	6.26	5.98	8.34	34.3

[1] HCO_3^- as mg m^{-2} yr^{-1} $CaCO_3$

be as great as 6-fold with a mean range of ~2-fold. Reporting on data from Hubbard Brook, N.H., Likens et al. (1977) found that export varied by as much as 19-fold between years over the 11 year study period. Most chemical species showed 2 to 3-fold ranges in export. In Sudbury, Nelson 3 had the greatest year-to-year variability in export for 14 of 19 chemical species (Mg^{2+}, Na^+, Cl^-, Cu and NO_3^- excepted). The reasons for this are not clear, although it is perhaps noteworthy that of the 5 hydrologically gauged headwater basins, Nelson 3 tended to have hydrologically distinct properties (Chapter 4). The greater amount of overburden in this watershed (Appendix 2) increased the water storage potential, possibly leading to increased interaction of water with the surficial materials.

Monthly export rates were calculated (Appendix 9) and in general, the same temporal patterns were observed for all 19 chemical species analysed. Monthly export followed the annual cycle of streamflow, being maximum in the period of spring runoff (March-May) and declining in June-September as streamflow decreased, showing a secondary peak in October-November and declining again in the winter. As the annual range in daily flow is 2-3 orders of magnitude as compared to a <1 order of magnitude range in concentration, this pattern is expected.

On a mass basis, SO_4^{2-}, Ca^{2+} and Si are the dominant substances being exported from the watersheds, except in Clearwater basins 2 and 4. In these basins, Cl^- is important because of the use of $CaCl_2$ in road maintenance. The range of exports for the 11 watersheds is compared in Table 5-9 to values for subwatersheds of Harp Lake in south central Ontario, Rawson Lake in N.W. Ontario and Hubbard Brook, New Hampshire. All of these additional watersheds are forested and underlain by silicate bedrock. As is the case for the

Table 5-9: Gross export (mg m^{-2} yr^{-1}) from Sudbury watersheds, watersheds of Harp Lake (south-central Ontario)[1], Rawson Lake (N.W. Ontario)[2], and Hubbard Brook (N.H.)[3]

	Sudbury				
	1977-1978	1978-1979	Harp Lake[1]	Rawson Lake[2]	Hubbard Brook[3]
H^+	0.81-26.5	1.64-18.5	0.33-3.71	0.14-9.9	11.4
Ca^{2+}	1620-6840	1900-6110	951-2300	264-830	1370
Mg^{2+}	363-1700	432-1050	276-627	118-302	313
Na^+	443-2580	612-2190	268-606	170-488	723
K^+	130-378	181-435	105-254	37-263	189
SO_4^{2-}	5700-15800	8520-15000	3200-6180	729-1485	5380
Cl^-	189-13700	210-11300	158-824	30-116	489
HCO_3^-	0-1790[4]	0-1640[4]	426-1950[4]	-	1250[4]
TP	3.13-7.58	3.88-8.85	-	2.0-11.0	2.3 (PO_4^{3-})
NO_3^-	4.72-72.1	9.60-60.3	4.77-416	-	386
NH_4^+	8.93-77.1	6.32-46.4	4.13-48.4	-	26.4
TKN	43.9-205	106-236	-	-	-
Si	1380-2680	1730-3830	-	777-2063	3840
Fe	46.0-703	59.2-396	-	58-162	-
Al	53.0-334	93.2-297	-	-	187
Mn	16.3-126	25.5-122	-	-	-
Cu	2.36-115	2.98-101	-	-	-
Ni	5.21-404	7.78-406	-	-	-
Zn	3.44-48.2	5.98-39.3	-	-	-

[1] Harvey _et_ _al_. 1981

[2] Schinder _et_ _al_. 1976

[3] Likens _et_ _al_. 1977

[4] HCO_3^- as mg m^{-2} yr^{-1} $CaCO_3$

Sudbury watersheds, SO_4^{2-}, Ca^{2+} and Si are the predominant substances exported from these watersheds. However, the export of H^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-} and Cl^- at Sudbury are all at the high end of the ranges for the other watersheds. This is the case even when the Clearwater 2 and 4 watersheds (containing roads) are excluded from the comparison, indicating elevated inputs and/or increased weathering in the Sudbury watersheds.

D. Net Export from Watershed

Annual net export from the watershed is defined as the difference between the gross export from the watershed and the input of material to the watershed in bulk precipitation. Tables 5-10 and 5-11 summarize the annual net exports for the 11 study watersheds for the periods June 1977 - May 1978 and June 1978 - May 1979, respectively. Negative values in the tables denote a net gain or retention of the chemical specie by the watershed. All basins exhibited a net export of Ca^{2+}, SO_4^{2-}, Mg^{2+} and Mn in both years. Ten of 11 basins showed a net loss of K^+ and Al in both years and 9 of 11 basins showed a net loss of Ni in both years. The remaining basins had a net gain of K^+, Al and Ni in June 1977 - May 1978 and a net loss in June 1978 - May 1979. Concentrations of Si in bulk deposition were commonly below the detection limit of the analytical method employed and thus the inputs to the watershed would be low. There was, therefore, a net export of Si from all watersheds in both years.

Total P, NO_3^-, NH_4^+, TKN and H^+ were retained by all basins in both periods and Zn was retained by 8 of 11 basins both

Table 5-10: Net export (mg m^{-2} yr^{-1}) from Sudbury watersheds for the period June 1977 - May 1978 inclusive.

	Clearwater				Nelson						Middle
	1	2	3	4	1	2	3	4	5	6	1
H^+	-52.1	-46.1	-54.6	-65.7	-48.9	-46.6	-61.7	-60.3	-62.4	-61.3	-61.4
Ca^{2+}	1240	6270	1170	2850	1570	1820	1130	2000	2320	1670	2830
Mg^{2+}	392	966	356	638	331	336	259	531	651	1600	1080
Na^+	-513	1460	-274	33.7	-238	-143	-319	-121	-139	-123	69.2
K^+	1.82	140	12.5	95.5	57.5	-15.5	10.2	91.7	165	126	296
$SO_4{}^{2-}$	4490	5570	4260	4340	4670	5500	2340	6080	6070	4220	11300
Cl^-	-53.6	13300	268	4080	-71.7	-97.7	-154	-89.6	-84.0	-121	906
HCO_3^-	45.8[1]	0.0	0.0	151[1]	18.6[1]	0.0	443[1]	581[1]	1790[1]	1230[1]	0.0
TP	-32.7	-34.2	-32.0	-31.2	-40.6	-42.9	-44.3	-42.7	-41.4	-44.4	-24.8
NO_3^-	-556	-541	-555	-548	-517	-544	-531	-537	-485	-521	-494
NH_4^+	-398	-398	-401	-348	-306	-308	-307	-310	-243	-311	-429
TKN	-588	-603	-555	-527	-526	-562	-582	-595	-493	-623	-546
Fe	81.6	-90.3	161	488	111	-58.9	-25.6	179	146	-3.03	-229
Al	113	294	186	285	79.6	140	3.76	36.9	-9.83	31.2	222
Mn	83.7	120	84.8	80.9	63.1	44.1	6.76	11.7	7.92	14.7	96.8
Cu	-66.6	-61.1	-66.4	-65.2	-41.2	-42.5	-43.6	-41.3	-42.5	-43.0	-182
Ni	31.5	94.0	17.2	44.3	10.3	8.85	-1.24	0.36	-0.24	5.58	294
Zn	-55.1	-18.5	-37.6	-41.3	-52.1	-47.9	-58.3	-57.5	-57.9	-57.0	- 24.6

[1] HCO_3^- as mg m^{-2} yr^{-1} $CaCO_3$

Table 5-11: Net export (mg m^{-2} yr^{-1}) from Sudbury watersheds for the period June 1978 - May 1979 inclusive.

	Clearwater				Nelson						Middle
	1	2	3	4	1	2	3	4	5	6	1
H^+	-42.0	-41.9	-44.3	-52.2	-38.4	-40.4	-53.4	-52.8	-55.4	-53.4	-48.0
Ca^{2+}	1690	5650	1440	3050	2090	2160	2170	3160	3290	2710	2820
Mg^{2+}	475	849	378	640	431	384	486	797	824	550	971
Na^+	186	1690	303	690	118	148	184	340	380	300	373
K^+	198	303	165	229	157	75.7	197	319	330	276	298
$SO_4{}^{2-}$	7100	6780	5980	5470	6740	6670	6070	10300	9510	7560	11400
Cl^-	-39.7	10900	116	4770	135	-10.5	67.8	94.0	100	515	717
HCO_3^-	53.4[1]	0.0	0.0	78.8[1]	39.8[1]	10.8[1]	743[1]	763[1]	1640[1]	909[1]	0.0
TP	-36.2	-37.8	-38.2	-37.3	-13.4	-17.9	-16.0	-15.5	-15.4	-18.2	-29.8
NO_3^-	-481	-487	-488	-474	-412	-450	-422	-443	-396	-424	-529
NH_4^+	-305	-312	-313	-283	-305	-325	-305	-318	-287	-319	-338
TKN	-419	-444	-439	-395	-297	-391	-353	-380	-300	-427	-450
Fe	171	103	212	312	259	-2.05	114	335	209	74.7	44.9
Al	163	233	158	254	175	175	98.8	89. 2	54.2	126	237
Mn	101	118	91.4	86.5	80.1	60.6	25.4	24.1	19.7	34.4	101
Cu	11.1	13.7	25.7	11.4	2.06	-0.93	-0.72	0.49	-0.61	-1.34	76.3
Ni	131	140	108	128	17.8	15.1	6.85	5.12	5.61	18.3	395
Zn	-9.63	13.4	-4.43	0.19	-14.8	-9.94	-20.0	-20.1	-20.3	-18.0	11.0

[1] HCO_3^- as mg m^{-2} yr^{-1} $CaCO_3$

years. Three basins (Clearwater 2, 4, and Middle 1) showed a net gain of Zn in 1977 - 1978 and a net loss in 1978 - 1979. Several chemical species showed a consistent pattern of net retention the first year and net loss the next. This pattern was common for Na^+ (8 of 11 basins), Cl^- (5 of 11 basins), Cu (7 of 11 basins) and Fe (4 of 11 basins).

Likens _et_ _al_. (1977) showed that data from one or a few annual cycles may give poor estimates of both the magnitude and the sign of net export (a positive sign indicating net export and a negative sign indicating net retention by the watershed). They note that the sign may be determined with confidence from 1-3 years of data for Ca^{2+}, Mg^{2+}, Na^+, Al, NH_4^+, H^+, SO_4^{2-}, HCO_3^- and Si. Potassium, NO_3^- and Cl^- required a greater number of years of data to determine with confidence whether the watershed exhibited a net gain or loss. The magnitude of the net export or retention could be reliably determined from a few (2-3) years data for Ca^{2+}, Mg^{2+}, Na^+, Al, NH_4^+, H^+, Si and HCO_3^- in the Hubbard Brook watershed. In this sense, the results of our 2 year study may in some cases be viewed as preliminary. Interpretation of our results was complicated by road construction operations which varied in intensity from year to year and the shutdown of Inco Ltd. (Chapter 2) during the 1978 - 1979 period. These factors, plus a consideration of the biogeochemical reactions in the watershed, can explain most of the results observed.

Total P, NO_3^-, NH_4^+, and TKN showed a net retention presumably because of biological uptake in the watershed. Weathering reactions are driven by the H^+ input and thus it is retained by the watershed, while the basic cations released by weathering include Ca^{2+}, Mg^{2+}, K^+, Mn and Al. The acid anion, SO_4, showed a net export from the watershed. The apparently large net export of SO_4^{2-} from the watersheds (gross export approximately 2-4 fold greater than input) is a reflection of the underestimation of the total SO_4^{2-} input as measured by bulk deposition. This is discussed in Chapters 2 and 8. The fact that the concentrations of Na^+ and Cl^- were near the detection limits of the analytical methods employed may explain their alternate net retention and loss by the watershed. In particular, there is evidence that the Na^+ concentrations in precipitation prior to June 1979 were systematically high (Chapter 2), explaining the retention of Na^+ by some watersheds in the period June 1977 - May 1978. None of the basins exhibiting the alternate retention and loss pattern had road building or maintenance operations within their boundaries (except Fe for Clearwater 2 and Middle 1) and thus such activities cannot be implicated. It may be significant that the shutdown of Inco Ltd. occurred in the year (1978 - 1979) that the watersheds showed a net loss of Cu. Although the gross export of Cu did not change appreciably between years, the input to the watershed decreased dramatically in the 1978 - 1979 period (Chapter 2). The watersheds which had the greatest reductions of Cu input were also those that showed a net retention in 1977 - 1978 and a net loss during the 1978 - 1979 period (Clearwater 1, 2, 3, 4, Middle 1 and Nelson 4).

An examination of net export on a monthly basis (Appendix 9) revealed 3 types of monthly patterns within a year: i) net retention by the watershed in all months, ii) net loss by the watershed in all months, and iii) a mixed or cross pattern of retention of the substance in some months and export in others. In 22 watershed-years of data, 11 watersheds for the 2-year period June 1977 - May 1979,

HCO_3^- was the only chemical species consistently lost in all months by all watersheds. No chemical species was consistently retained on a monthly basis by any watershed. However, H^+, NO_3^-, NH_4^+, and TKN were retained in all months in most watershed-years (17 of 22 for H^+, 21 of 22 for NO_3^-, 20 of 22 for NH_4^+, 15 of 22 for TKN), with some watersheds showing cross patterns for some years. All other chemical species exhibited cross patterns. Likens et al. (1977) noted that Mg^{2+}, Ca^{2+}, Na^+ and Al were lost from the Hubbard Brook watershed each month if data for 11 years were averaged. Hydrogen ion, NH_4^+ and PO_4^{3-} were retained each month and K^+, SO_4^{2-}, NO_3^- and Cl^- exhibited cross patterns.

In general, those chemical species with cross patterns were lost by the watershed in the spring and fall period when runoff was high. Net retention occurred in the summer months when streamflow was low (or zero) and sometimes in the winter, probably because the input to the watershed was held in the snowpack. Water itself showed a cross pattern.

An alternate way of evaluating the net export data is in terms of watershed assimilation, or the ability of a watershed to retain inputs of material expressed in terms of a retention coefficient.

$$\text{Retention coefficient} = \frac{\text{input} - \text{gross export}}{\text{input}} \qquad (5\text{-}2)$$

This unitless coefficient is related to net export (= negative net export/input) but, in addition, provides information on the relative magnitude of the input and gross export values. The retention coefficient approaches a value of 1 for those parameters which are strongly retained by the watershed (e.g. gross export <<input), and a value of 0 for parameters whose gross export equals input. A negative coefficient implies that the watershed is acting as a source, with a value of -1 showing that gross export exceeds input by 2-fold, a value of -2 showing that gross export exceeds input by 3-fold, etc. Retention coefficients for 11 experimental watersheds for June 1977 to May 1978, and June 1978 to May 1979 are given in Tables 5-12 and 5-13, respectively.

A summary of net export data for watersheds in several areas of the world is presented in Likens et al. (1977). The net export of material from the Sudbury watersheds is compared to that of subwatersheds of Harp Lake (south-central Ontario), Rawson Lake (N.W. Ontario) and Hubbard Brook (N.H.) in Table 5-14. Even excluding the watersheds in Sudbury affected by road construction and maintenance activities, the net exports of Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} from the Sudbury watersheds were at the high end of the ranges shown, indicative of elevated input and/or increased weathering. The net export of Al is similar to that at Hubbard Brook. Roughly equal amounts of H^+ were retained by watersheds at Sudbury and Harp Lake, both retaining less H^+ than Hubbard Brook on an absolute basis. The net retention of NO_3^- and NH_4^+ was greater in the Sudbury watersheds than at Hubbard Brook.

E. Acid-Base Balance

As previously discussed, the weathering of silicate rock terrains may be considered an acid-base reaction between atmospherically supplied acids and lithologic bases. Associated with the consumption of acid is the release of an equivalent quantity of basic cations. By considering the components of the net acid supply

Table 5-12: Retention coefficients for ions, nutrients, and heavy metals for 11 watersheds near Sudbury for the period June 1977 to May 1978. Coefficients were calculated using bulk deposition as input.

	Watershed										
	Clearwater				Nelson						Middle
Parameter	1	2	3	4	1	2	3	4	5	6	1
H^+	0.72	0.64	0.75	0.90	0.77	0.74	0.98	0.95	0.99	0.97	0.79
Ca^{2+}	-2.2	-11	-2.0	-4.9	-3.2	-3.8	-2.3	-4.1	-4.8	-3.4	-3.4
Mg^{2+}	-4.9	-12	-4.4	-8.0	-3.2	-3.2	-2.5	-5.1	-6.2	-15	-11
Na^+	0.46	-1.3	0.24	-0.03	0.31	0.19	0.42	0.16	0.18	0.16	-0.07
K^+	-0.01	-0.59	-0.05	-0.40	-0.40	0.11	-0.07	-0.63	-1.14	-0.87	-2.4
SO_4^{2-}	-1.1	-1.4	-1.1	-1.1	-1.4	-1.6	-0.70	-1.8	-1.8	-1.3	-2.5
Cl^-	0.13	-33	-0.67	-10.2	0.21	0.29	0.45	0.26	0.25	0.35	-1.8
TP	0.84	0.88	0.83	0.80	0.86	0.90	0.93	0.90	0.87	0.93	0.82
NO_3^-	0.97	0.94	0.97	0.95	0.94	0.99	0.97	0.98	0.88	0.95	0.87
NH_4^+	0.97	0.97	0.98	0.85	0.96	0.96	0.96	0.97	0.76	0.97	0.94
TKN	0.80	0.83	0.76	0.72	0.76	0.82	0.85	0.86	0.72	0.90	0.78
Fe	-0.38	0.42	-0.75	-2.3	-1.1	0.56	0.24	-1.7	-1.4	0.03	0.57
Al	-2.8	-7.2	-4.6	-7.0	-1.3	-2.2	-0.06	-0.59	0.16	-0.50	-4.2
Mn	-14	-20	-14	-13	-6.6	-4.6	-0.71	-1.2	-0.83	-1.5	-13
Cu	0.76	0.70	0.76	0.75	0.91	0.94	0.96	0.91	0.94	0.95	0.61
Ni	-0.39	-1.2	-0.21	-0.54	-1.6	-1.4	0.19	-0.06	0.04	-0.89	-2.7
Zn	0.83	0.28	0.56	0.62	0.85	0.78	0.95	0.94	0.94	0.93	0.51

Table 5-13: Retention coefficients for ions, nutrients, and heavy metals for 11 watersheds near Sudbury for the period June 1978 to May 1979. Coefficients were calculated using bulk deposition as input.

	Watershed										
	Clearwater				Nelson						Middle
Parameter	1	2	3	4	1	2	3	4	5	6	1
H^+	0.69	0.69	0.73	0.86	0.67	0.71	0.94	0.93	0.97	0.94	0.81
Ca^{2+}	-3.7	-12	-3.2	-6.7	-4.8	-5.0	-5.0	-7.3	-7.6	-6.3	-4.6
Mg^{2+}	-7.9	-14	-6.3	-11	-9.0	-8.0	-10	-17	-17	-11	-12
Na^+	-0.37	-3.3	-0.59	-1.4	-0.24	-0.30	-0.37	-0.69	-0.77	-0.61	-0.58
K^+	-1.8	-2.8	-1.5	-2.1	-1.5	-0.72	-1.9	-3.0	-3.1	-2.6	-3.2
SO_4^{2-}	-2.3	-2.2	-2.0	-1.8	-2.1	-2.1	-1.9	-3.2	-3.0	-2.4	-3.1
Cl^-	0.12	-32	-0.34	-14	-0.61	0.05	-0.31	-0.43	-0.45	-2.3	-1.7
TP	0.86	0.90	0.91	0.89	0.60	0.81	0.72	0.70	0.69	0.82	0.85
NO_3^-	0.97	0.98	0.98	0.95	0.90	0.99	0.92	0.97	0.87	0.93	0.92
NH_4^+	0.95	0.98	0.98	0.89	0.91	0.97	0.92	0.95	0.86	0.96	0.93
TKN	0.73	0.77	0.76	0.69	0.56	0.73	0.66	0.71	0.56	0.81	0.77
Fe	-2.5	-1.5	-3.1	-4.5	-4.2	0.03	-1.9	-5.5	-3.4	-1.2	-0.42
Al	-4.0	-5.8	-3.9	-6.3	-4.5	-4.5	-2.5	-2.3	-1.4	-3.2	-4.0
Mn	-23	-26	-20	-19	-14	-11	-4.4	-4.2	-3.4	-6.0	-18
Cu	-1.2	-1.5	-0.28	-1.3	-0.56	0.25	0.20	-0.13	0.17	-0.36	-3.0
Ni	-29	-32	-24	-29	-6.7	-5.7	-2.6	-1.9	-2.1	-6.9	-35
Zn	0.37	-0.52	0.17	-0.01	0.56	0.38	0.76	0.76	0.77	0.68	-0.47

Table 5-12: Retention coefficients for ions, nutrients, and heavy metals for 11 watersheds near Sudbury for the period June 1977 to May 1978. Coefficients were calculated using bulk deposition as input.

	Watershed										
	Clearwater				Nelson						Middle
Parameter	1	2	3	4	1	2	3	4	5	6	1
H^+	0.72	0.64	0.75	0.90	0.77	0.74	0.98	0.95	0.99	0.97	0.79
Ca^{2+}	-2.2	-11	-2.0	-4.9	-3.2	-3.8	-2.3	-4.1	-4.8	-3.4	-3.4
Mg^{2+}	-4.9	-12	-4.4	-8.0	-3.2	-3.2	-2.5	-5.1	-6.2	-15	-11
Na^+	0.46	-1.3	0.24	-0.03	0.31	0.19	0.42	0.16	0.18	0.16	-0.07
K^+	-0.01	-0.59	-0.05	-0.40	-0.40	0.11	-0.07	-0.63	-1.14	-0.87	-2.4
SO_4^{2-}	-1.1	-1.4	-1.1	-1.1	-1.4	-1.6	-0.70	-1.8	-1.8	-1.3	-2.5
Cl^-	0.13	-33	-0.67	-10.2	0.21	0.29	0.45	0.26	0.25	0.35	-1.8
TP	0.84	0.88	0.83	0.80	0.86	0.90	0.93	0.90	0.87	0.93	0.82
NO_3^-	0.97	0.94	0.97	0.95	0.94	0.99	0.97	0.98	0.88	0.95	0.87
NH_4^+	0.97	0.97	0.98	0.85	0.96	0.96	0.96	0.97	0.76	0.97	0.94
TKN	0.80	0.83	0.76	0.72	0.76	0.82	0.85	0.86	0.72	0.90	0.78
Fe	-0.38	0.42	-0.75	-2.3	-1.1	0.56	0.24	-1.7	-1.4	0.03	0.57
Al	-2.8	-7.2	-4.6	-7.0	-1.3	-2.2	-0.06	-0.59	0.16	-0.50	-4.2
Mn	-14	-20	-14	-13	-6.6	-4.6	-0.71	-1.2	-0.83	-1.5	-13
Cu	0.76	0.70	0.76	0.75	0.91	0.94	0.96	0.91	0.94	0.95	0.61
Ni	-0.39	-1.2	-0.21	-0.54	-1.6	-1.4	0.19	-0.06	0.04	-0.89	-2.7
Zn	0.83	0.28	0.56	0.62	0.85	0.78	0.95	0.94	0.94	0.93	0.51

Table 5-13: Retention coefficients for ions, nutrients, and heavy metals for 11 watersheds near Sudbury for the period June 1978 to May 1979. Coefficients were calculated using bulk deposition as input.

	Watershed										
	Clearwater				Nelson						Middle
Parameter	1	2	3	4	1	2	3	4	5	6	1
H^+	0.69	0.69	0.73	0.86	0.67	0.71	0.94	0.93	0.97	0.94	0.81
Ca^{2+}	-3.7	-12	-3.2	-6.7	-4.8	-5.0	-5.0	-7.3	-7.6	-6.3	-4.6
Mg^{2+}	-7.9	-14	-6.3	-11	-9.0	-8.0	-10	-17	-17	-11	-12
Na^+	-0.37	-3.3	-0.59	-1.4	-0.24	-0.30	-0.37	-0.69	-0.77	-0.61	-0.58
K^+	-1.8	-2.8	-1.5	-2.1	-1.5	-0.72	-1.9	-3.0	-3.1	-2.6	-3.2
SO_4^{2-}	-2.3	-2.2	-2.0	-1.8	-2.1	-2.1	-1.9	-3.2	-3.0	-2.4	-3.1
Cl^-	0.12	-32	-0.34	-14	-0.61	0.05	-0.31	-0.43	-0.45	-2.3	-1.7
TP	0.86	0.90	0.91	0.89	0.60	0.81	0.72	0.70	0.69	0.82	0.85
NO_3^-	0.97	0.98	0.98	0.95	0.90	0.99	0.92	0.97	0.87	0.93	0.92
NH_4^+	0.95	0.98	0.98	0.89	0.91	0.97	0.92	0.95	0.86	0.96	0.93
TKN	0.73	0.77	0.76	0.69	0.56	0.73	0.66	0.71	0.56	0.81	0.77
Fe	-2.5	-1.5	-3.1	-4.5	-4.2	0.03	-1.9	-5.5	-3.4	-1.2	-0.42
Al	-4.0	-5.8	-3.9	-6.3	-4.5	-4.5	-2.5	-2.3	-1.4	-3.2	-4.0
Mn	-23	-26	-20	-19	-14	-11	-4.4	-4.2	-3.4	-6.0	-18
Cu	-1.2	-1.5	-0.28	-1.3	-0.56	0.25	0.20	-0.13	0.17	-0.36	-3.0
Ni	-29	-32	-24	-29	-6.7	-5.7	-2.6	-1.9	-2.1	-6.9	-35
Zn	0.37	-0.52	0.17	-0.01	0.56	0.38	0.76	0.76	0.77	0.68	-0.47

Table 5-14: Net export (mg m^{-2} yr^{-1}) from Sudbury watersheds, watersheds of Harp Lake (south-central Ontario)[1], Rawson Lake (N.W. Ontario)[2] and Hubbard Brook (N.H.)[3]

	Sudbury 1977-1978	Sudbury 1978-1979	Harp Lake[1]	Rawson Lake[2]	Hubbard Brook[3]
H^+	-65.7-(-46.1)	-55.4-(-38.4)	-81.8-(-52.5)	-11.1-2.0	-87.2
Ca^{2+}	1130-6270	1440-5650	257-1784	-118-498	1160
Mg^{2+}	259-1600	378-971	196-551	45-209	255
Na^+	-513-1460	118-1690	-171-368	35-305	564
K^+	-15.5-296	75.7-330	-49.7-150	-95-158	99
$SO_4{}^{2-}$	2340-11300	5470-11400	-239-2957	-59-190	1530
Cl^-	-154-13300	-39.7-10900	-139-604	105-171	-202
$HCO_3{}^-$	0-1790[4]	0-1640[4]	-	-	1250[4]
TP	-44.4-(-24.8)	-38.2-(-13.4)	-	-46-(-14)	-
$NO_3{}^-$	-556-(-485)	-529-(-396)	-501-(-118)	-	-58.8
$NH_4{}^+$	-429-(-243)	-338-(-283)	-542-(-326)	-	-197
TKN	-623-(-493)	-450-(-297)	-	-	-
Si	-	-	-	755-2030	-
Fe	-229-488	-2.05-335	-	-	-
Al	-9.83-294	54.2-254	-	-	187
Mn	6.76-120	19.7-118	-	-	-
Cu	-182-(-41.2)	-1.34-76.3	-	-	-
Ni	-1.24-294	5.12-395	-	-	-
Zn	-58.3-(-18.5)	-20.3-13.4	-	-	-

[1] Harvey _et_ _al_. 1981

[2] Schindler _et_ _al_. 1976

[3] Likens _et_ _al_. 1977

[4] $HCO_3{}^-$ as mg m^{-2} yr^{-1} $CaCO_3$

and net base release, it is possible to determine whether natural or anthropogenic sources of acid are the primary driving force for weathering reactions (Harvey et al. 1981).

Tables 5-15, 5-16 and 5-17 summarize the net acid supply and consumption by the 11 watersheds for the periods June 1977 - May 1978, June 1978 - May 1979 and June 1977 - Dec. 1979, respectively. We have data on three components of the acid supply. First, H^+ is supplied from the atmosphere in precipitation and the net H^+ retention by the watershed is a component of the acid supply. Second, we equate the net export of HCO_3^- to an equivalent supply of acid produced by the dissociation of H_2CO_3, probably in the soil environment. This assumes that no additional source of HCO_3^- is present in the watershed (carbonate bedrock or carbonate materials in surficial deposits). The assumption is valid for the 11 watersheds under study (Appendix 2c). Also, atmospheric deposition of HCO_3^- is negligible due to the consistently low pH of the precipitation (Chapter 2). Third, we assume that the NH_4^+ introduced to the watershed by precipitation is an acidifying substance. The uptake of NH_4^+ by biological processes results in the release of an H^+ ion to the soil (Reuss 1976). Therefore, the net retention of NH_4^+ (meq m^{-2} yr^{-1}) by the watershed is a component of the total acid supply. Of the measured acid inputs, $H^+ > NH_4^+ > HCO_3^-$ in both years for all watersheds, except Nelson 5 ($H^+ > HCO_3^- > NH_4^+$).

Balanced against the above sources of acid supply are the substances produced or liberated by acid-consuming reactions. These include basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and other metals (noteably Al). Nitrate can also be an acid-consuming substance,

Table 5-15: Net acid supply and consumption (meq m^{-2} yr^{-1}) in 11 watersheds at Sudbury from June 1977 - May 1978. Acid supply includes net watershed gain of H^+, NH_4^+ and loss of HCO_3^- Acid consumption is reflected by net watershed loss of Ca^{2+}, Mg^{2+}, Na^+, K^+, and Al^{3+}, and net gain of NO_3^-.

Watershed	Net Acid Supply H^+	NH_4^+	HCO_3^-	Sum	Net Acid Consumption Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	NO_3^-	Sum	Ratio[2]
Clearwater 1	52.1	28.4	0.92	81.4	61.9	32.3	-22.4	0.05	12.6	39.7	124	0.657
Clearwater 2	46.1	28.4	0.00	74.5	313[1]	79.4	63.7[1]	3.57	32.7	38.7	155[1]	0.481[1]
Clearwater 3	54.6	28.7	0.00	83.3	58.2	29.3	-12.0	0.32	20.7	39.7	136	0.612
Clearwater 4	65.7	24.8	3.02	93.5	142[1]	52.4	1.5[1]	2.44	31.7	39.1	154[1]	0.607[1]
Middle 1	61.4	30.7	0.00	92.1	141	88.6	3.01	7.57	24.7	35.3	300	0.307
Nelson 1	48.9	21.8	0.20	70.9	78.4	27.2	-10.4	1.47	8.85	36.9	143	0.496
Nelson 2	46.6	22.0	0.00	68.6	91.0	27.6	-6.2	-0.40	15.6	38.9	167	0.412
Nelson 3	61.7	21.9	8.86	92.5	56.5	21.3	-13.9	0.26	0.42	37.9	103	0.898
Nelson 4	60.3	22.1	11.6	94.0	100	43.6	-5.25	2.35	4.10	38.4	183	0.514
Nelson 5	62.4	17.3	35.8	116	116	53.5	-6.05	4.23	-1.09	34.6	201	0.577
Nelson 6	61.3	22.2	24.6	108	83.1	131	-5.33	3.24	3.47	37.2	253	0.427

[1] Ca^{2+} and Na^+ net export values for Clearwater 2 and 4 include contributions from road chemicals which are associated with an equal net export of Cl^-; therefore, the sum of acids consumed has been estimated by subtracting Cl^- net export

[2] Ratio = Sum acid supply/Sum acid consumed

Table 5-16: Net acid supply and consumption (meq m^{-2} yr^{-1}) in 11 watersheds at Sudbury from June 1978 – May 1979. Acid supply includes net watershed gain of H^+, NH_4^+ and loss of HCO_3^-. Acid consumption is reflected by net watershed loss of Ca^{2+}, Mg^{2+}, Na^+, K^+, and Al^{3+}, and net gain of NO_3^-.

	Net Acid Supply				Net Acid Consumption							
Watershed	H^+	NH_4^+	HCO_3^-	Sum	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	NO_3^-	Sum	Ratio[2]
Clearwater 1	42.0	21.8	1.06	64.9	84.2	39.1	8.13	5.06	18.1	34.4	189	0.343
Clearwater 2	41.9	22.3	0.00	64.3	282[1]	69.8	73.6[1]	7.74	25.9	34.8	186[1]	0.346[1]
Clearwater 3	44.3	22.4	0.00	66.7	72.1	31.1	13.2	4.22	17.6	34.8	173	0.386
Clearwater 4	52.2	20.2	1.58	73.9	152	52.6	30.1[1]	5.86	28.3	33.8	168[1]	0.440[1]
Middle 1	48.0	24.1	0.00	72.1	141	79.9	16.2	7.61	26.4	37.8	309	0.233
Nelson 1	38.4	21.8	0.71	60.9	104	35.5	5.13	4.02	19.5	29.4	198	0.308
Nelson 2	40.4	23.2	0.00	63.6	108	31.6	6.45	1.94	19.5	32.1	200	0.318
Nelson 3	53.4	21.8	14.9	90.1	108	40.0	8.01	5.04	11.0	30.1	202	0.446
Nelson 4	52.8	22.7	15.3	90.8	158	65.6	14.8	8.15	9.92	31.6	288	0.315
Nelson 5	55.4	20.5	32.8	109	164	67.7	16.5	8.44	6.03	28.3	291	0.375
Nelson 6	53.4	22.8	18.2	94.4	135	45.2	13.1	7.06	14.0	30.3	245	0.385

[1] Ca^{2+} and Na^+ net export values for Clearwater 2 and 4 include contributions from road chemicals which are associated with an equal net export of Cl^-; therefore, the sum of acids consumed has been estimated by subtracting Cl^- net export

[2] Ratio = Sum acid supply/Sum acid consumed

Table 5-17: Net acid supply and consumption (meq m^{-2} yr^{-1}) in 11 watersheds at Sudbury from June 1977 - Dec. 1979. Acid supply includes net watershed gain of H^+, NH_4^+ and loss of HCO_3^-. Acid consumption is reflected by net watershed loss of Ca^{2+}, Mg^{2+}, Na^+, K^+, and Al^{3+}, and net gain of NO_3^-.

	Net Acid Supply				Net Acid Consumption							
Watershed	H^+	NH_4^+	HCO_3^-	Sum	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	NO_3^-	Sum	Ratio[2]
Clearwater 1	123	64.2	1.92	189	188	89.6	7.1	4.7	36.4	95.0	420	0.450
Clearwater 2	116	64.7	0.00	181	787[1]	195	172[1]	13.2	68.5	94.2	443[1]	0.409[1]
Clearwater 3	129	65.2	0.00	194	150	70.1	11.4	5.8	43.8	95.0	377	0.515
Clearwater 4	151	58.0	5.00	214	337[1]	123	49.6[1]	10.3	67.7	92.9	500[1]	0.428[1]
Middle 1	137	70.1	0.00	207	332	198	32.9	17.8	52.5	92.9	727	0.285
Nelson 1	127	60.4	0.91	188	219	73.4	-0.3	6.1	33.6	85.0	417	0.453
Nelson 2	128	62.6	0.00	191	226	67.6	6.4	1.8	41.6	90.0	434	0.440
Nelson 3	159	59.4	26.4	245	221	79.6	3.6	7.3	13.7	85.0	410	0.598
Nelson 4	157	62.1	33.4	253	301	127	17.8	12.2	16.8	89.3	564	0.449
Nelson 5	163	54.7	79.2	297	319	137	18.5	15.0	5.5	81.4	576	0.516
Nelson 6	159	62.4	48.6	270	255	191	26.7	12.6	20.2	85.7	591	0.457

[1] Ca^{2+} and Na^+ net export values for Clearwater 2 and 4 include contributions from road chemicals which are associated with an equal net export of Cl^-; therefore, the sum of acids consumed has been estimated by subtracting Cl^- net export

[2] Ratio = Sum acid supply/Sum acid consumed

since biological uptake of atmospherically supplied NO_3^- may result in the release of an equivalent quantity of OH^- (or HCO_3^-) to the soil (Reuss 1976). The assessment of net Al export as an indicator of acid consumption is complicated by the fact that the actual species exported has not been determined. We assume that Al is in the Al^{3+} form, and probably overestimate the H^+ consumed as a result. The error is potentially greatest for streams with higher pH because the proportion of Al as Al^{3+} decreases as pH increases. However, the error is minimized because Al export decreases (relative to other cations) as H^+ export decreases (and stream pH increases). Watersheds with the highest Al export are drained by streams of low pH wherein the greatest proportion of Al is as Al^{3+}.

In order to estimate the component of the Ca^{2+} and Na^+ net export associated with acid consumption for those watersheds affected by road maintenance activities ($CaCl_2$ and NaCl were added to roads in Clearwater 2 and 4), the net export of Cl^- was subtracted from the sum of the net acids consumed in Tables 5-15, 5-16 and 5-17. This correction assumes that the only source of Cl^- is from the use of NaCl and $CaCl_2$. If this assumption is correct, the net Cl^- export from Clearwater 1 and 3 watersheds and the Nelson watersheds which do not contain roads should be zero. In fact, except for Clearwater 3 in 1978 - 1979 and Nelson 6 in 1978 - 1979 the net Cl^- export was close to zero (-4.35 to 3.81 meq m^{-2} yr^{-1}).

The ratio of the total net acids supplied to the total net acids consumed was <1 in all periods (Tables 5-15, 5-16, 5-17), ranging from 0.90 (Nelson 3, 1977-1978) to 0.23 (Middle 1, 1978 - 1979), indicating that we have failed to measure all the acid inputs to the watersheds. The large net export of SO_4^{2-} from the watersheds indicates that the principal "missing" acidifying substance is SO_2. Compared to values in 1977 - 1978, the measured net supply of acids decreased in the 1978 - 1979 period which contained the 8 months when Inco Ltd. was shut down. The unmeasured SO_2 input also decreased during the shutdown period (Chapter 2). However, even though the net acid supply decreased in 1978 - 1979, the net acid consumption did not. This suggests that the net export figures reflect a long-term integration of factors by the watersheds.

It is reasonable to consider the movement of materials within a watershed as a chromatographic process. Ions which are carried from the location of initial weathering to the stream undergo a series of adsorption/desorption reactions as the carrier solution (runoff water) percolates through the litter and soils of the watershed. The rate of ion movement will consequently be very much slower than the rate of water movement through the watershed. Within this conceptual framework, there is no reason to expect a simple short-term cause and effect response explaining the measured net exports, (eg. reduced acid inputs being immediately reflected by reduced net export of cations). Such a time-integrated response would be a function of the quantity of runoff moving through the system, which may partially explain the consistently different ratios in Tables 5-15 and 5-16 since 17% more precipitation was recorded in the 1978-1979 year compared to the 1977 - 1978 year.

The unmeasured SO_2 inputs can be estimated by calculating a deposition rate using estimated air concentrations (Chapter 2) and deposition velocity, or by assuming that the net SO_4^{2-} export is a result of unmeasured SO_2 inputs (Table 5-18). The method

Table 5-18: Estimated acid input (meq m^{-2} $period^{-1}$) from the dry deposition of SO_2 to watersheds in the Sudbury area for June 1977 - May 1978; June 1978 - May 1979; and June 1977 - December 1979. Estimates were derived a) from multiplying average monthly SO_2 concentrations by a deposition velocity of 0.8 cm sec^{-1} (Garland 1978) and summing, and b) from the areally-weighted average net export of SO_4^{2-} from the subwatersheds of each lake basin (see text). Measured areally-weighted average acid supply and consumption (derived from Tables 5-15 to 5-17) and acid deficiency[3] are included for comparison.

		Watersheds		
Period	Acid	Clearwater	Middle	Nelson
June 1977 -May 1978	Estimated Input from Air Concentration[1]	70	95	70
	Estimated Input from Net SO_4^{2-} Export[2]	94.9	235	99.8
	Measured Acid Supply	84.6	92.1	90.0
	Measured Acid Consumption	139	300	160
	Acid Deficiency[3]	54.4	208	70
June 1978 -May 1979	Estimated Input from Air Concentration[1]	30	80	35
	Estimated Input from Net SO_4^{2-} Export[2]	133	238	162
	Measured Acid Supply	67.9	72.1	83.8
	Measured Acid Consumption	180	309	235
	Acid Deficiency[3]	113	237	151
June 1977 -December 1979	Estimated Input from Air Concentration[1]	120	220	130
	Estimated Input from Net SO_4^{2-} Export[2]	269	536	292
	Measured Acid Supply	197	207	238
	Measured Acid Consumption	444	727	481
	Acid Deficiency[3]	247	520	243

[1] SO_2 deposition for Clearwater calculated using air concentrations from Burwash; for Middle from the average of Lockerby and Ash concentration; and for Nelson from the average of Rayside and Hamner concentrations (SO_2 concentrations provided by the Northeastern Region, Ontario Ministry of the Environment).

[2] SO_2 deposition for Clearwater obtained by calculating areally-weighted average net SO_4^{2-} export from 4 subwatersheds; for Middle, from 1 subwatershed; and for Nelson, from 6 subwatersheds.

[3] Acid deficiency = areally-weighted average acid consumption - areally-weighted average acid supply from Tables 5-15 to 5-17.

assumes that there is no other sulphur source in the watersheds, while both assume that all SO_2 deposited is oxidized to SO_4^{2-}. Estimates derived from the first approach are limited by a lack of accurate air concentration data for our watersheds, while for the second method, both the peat bogs and Onaping tuffs, and breccia (at Nelson Lake, Appendix 2c) might act as sources of SO_4^{2-}. Also, a time-integration effect similar to that discussed above for cation export, may exist for SO_4^{2-}, although anions are generally considered to be more mobile (less strongly adsorbed) in the soil environment than cations (Bolt and Bruggenwert 1978). Also included in Table 5-18 is the measured acid supply and consumption (areally weighted averages). The estimated unmeasured input of SO_2 by dry deposition may then be compared to the apparent deficiency in acid supply for the watersheds.

In all cases, the estimate of SO_2 inputs by dry deposition derived from net SO_4^{2-} export exceeds estimates calculated from monthly average air concentrations. The difference is greater than 2-fold for all the periods considered, except for Clearwater and Nelson Lakes between June 1977 and May 1978. This may result from either a lack of accurate air concentration data for the specific watersheds, or possibly from the use of an inappropriately low value for the SO_2 deposition velocity (0.8 cm sec^{-1}; Garland 1978). The first limitation is probably more important since large gradients in SO_2 concentrations have been measured in the Sudbury area (Table 2-23). In particular air concentration data for two nearby monitoring stations were averaged for each of the Middle and Nelson Lake watersheds, and a 2-fold variation in concentration between these pairs of stations was often observed. The greatest absolute difference was observed for the SO_2 stations used for the Middle

Lake watershed closest to the smelters (eg. Lockerby and Ash; calculated deposition = 140 and 300 meq m^{-2}, respectively, for June 1977 to December 1979). The "SO_4^{2-} export" approach has the advantage that the integrated response of the watershed itself is used to estimate SO_2 deposition.

The data in Table 5-18, also show that SO_2 input by dry deposition may constitute a major component of the total acid supply to the watersheds. Considering the "SO_4^{2-} export" estimate for the 31 month time period, the dry input is slightly greater than the sum of all other measured inputs at Clearwater and Nelson (1.4- and 1.2-fold, respectively), while at Middle, the dry fraction clearly predominates, being 2.6-fold greater than the measured inputs.

Acid-base balances, weighted by area for the watersheds used are presented in Table 5-19. These balances include an estimate of the dry deposition of acid obtained from SO_2 concentrations in air. The percent balance improved with the additional acid dry deposition term, however, the total acid supply still remained less than the measured acid consumption, except for the Clearwater and Nelson watersheds in 1977-78. The dry acid deposition is underestimated for the reasons discussed above.

Although very good balances may be obtained by including dry acid deposition estimated from the net watershed export of SO_4^{2-}, this is not an independent test of the acid-base balance. A balance obtained in this manner is essentially a charge balance calculation since the exports of Cl^- are small compared to those of the other ions.

Table 5-19: Percent acid-base balance[1] for the Clearwater, Middle and Nelson watersheds for June 1977 - May 1978; June 1978 - May 1979; and June 1977 - December 1979. Percent acid balance[1] for measured acid supply and consumption (Table 5-15, 5-16, 5-17) is presented as well as cases where estimates of the dry deposition of SO_2 are included in the acid supply term.

Period	Acid Supply Considered	Acid-Base Balance[1] (%) Clearwater	Middle	Nelson
June 1977 -May 1978	Measured	61	31	56
	incl. SO_2 estim. from air conc.	111	62	100
June 1978 -May 1979	Measured	38	23	36
	incl. SO_2 estim. from air conc.	54	49	51
June 1977 -December 1979	Measured	44	28	49
	incl. SO_2 estim. from air conc.	71	59	77

[1] Acid-base balance = $\frac{\text{Areally weighted average acid supply}}{\text{Areally weighted average acid consumption}} \times 100$

(areally weighted averages from Tables 5-15, 5-16, 5-17).

F. Summary

1. The factors controlling stream chemistry and the export of materials from watersheds were examined in 11 headwater watersheds of Middle, Clearwater and Nelson Lakes. The mean concentrations of H^+, Ca^{2+}, Cl^-, NO_3^-, NH_4^+, Cu, Ni and Zn varied more than 10-fold between streams. With a few exceptions, temporal variation was generally small for major ions (<10-fold) and large (>10-fold) for nutrients, Cu, Ni and Zn. All variations in concentration were small compared to variations in flow within a stream.
2. The dominance of SO_4^{2-} and absence of HCO_3^- in most streams suggested that mineral weathering in the Sudbury area is primarily driven by the input of strong acids, rather than by the dissociation of carbonic acid as occurs in watersheds not affected by anthropogenic activities. The order of cation dominance ($Ca^{2+} > Mg^{2+} > Na^+ > K^+$) in the streams is in general agreement with that expected for felsic geochemical environments.
3. Stepwise multi-linear regression was used to quantify relationships between physical and geological characteristics of the 11 watersheds and their associated stream chemistry. The presence of roadways and the types of surficial deposits in the watersheds were generally the most important characteristics explaining stream concentration.
4. Great variability in gross export was observed for the 19 chemical species analyzed and could largely be explained on the basis of geology or the existence of roadways in the watershed. On a mass basis, SO_4^{2-}, Ca^{2+} and Si were the dominant substances exported. In general, material export from Sudbury

watersheds is at the high end of the ranges reported for Shield watersheds underlain by silicate bedrock.

5. The watersheds generally exhibited positive values of net export (gross export-input) for Ca^{2+}, SO_4^{2-}, Mg^{2+}, Mn, K^+, Al, Ni, and Si. Total P, NO_3^-, NH_4^+, TKN and H^+ were consistently retained within the watersheds, while Na^+, Cl^-, Cu, and Fe gave different results in different years. These differences were attributable to the biogeochemical reactions in the watersheds of the substances, and/or to varying inputs of materials to the watersheds. Net export of ions at Sudbury was generally at the high end of the range reported elsewhere for watersheds underlain by silicate bedrock.
6. When net export for the 11 watersheds was examined on a monthly basis, different patterns were apparent for different substances. Only alkalinity was consistently lost from the watersheds in all months of the study, while in contrast, H^+, NO_3^-, NH_4^+ and TKN were retained in almost all watersheds at all times. All other chemical species exhibited "cross-patterns", eg. having net loss in spring and fall, and net retention in summer and sometimes winter.
7. The source of acid (natural or anthropogenic) driving weathering reactions in the 11 watersheds at Sudbury was assessed by considering the components of acid supply and consumption. Consistently more acid was consumed by the watersheds than was apparently supplied. The "missing" or unmeasured acid supply was inferred to be SO_2 deposited during dry periods, since a) the atmospheric deposition of this parameter was known to be an underestimate (see Chapter 2), and b) the watersheds exhibited

large net export of SO_4^{2-}, despite the fact that no readily apparent source of S was present within them. These results show that anthropogenically-supplied strong acids are the dominant driving force for weathering at Sudbury, and that the dry deposition of SO_2 is 1.2- to 2.6-fold greater than the sum of all other measured acid inputs.

LIST OF FIGURES

Fig. 5-1. Aqueous aluminum in equilibrium with gibbsite (from May *et al*. 1979).

Fig. 5-2. Predominance diagrams illustrating the stability relations of some mineral phases, calculated using equilibrium constants given in Table 8-4 of Stumm and Morgan (1970). In typical weathering regimes, feldspars are converted to either kaolinite, or montmorillonite (if H_4SiO_4 concentration are high). Conversion of feldspar to clay minerals is favoured by low aqueous concentrations of Na^+, Ca^{++}, K^+ and high H^+ concentrations. Solid dots are Sudbury area streams. Other data from Table 5-2 are included for comparison: #1 = Muskoka-Haliburton, #2 = Hubbard Brook, #3 = Sierra Nevada (ephemeral streams), #4 = Sierra Nevada (perennial streams), and #5 = streams draining into Rawson Lake, Experimental Lakes Area.

Fig.5-1

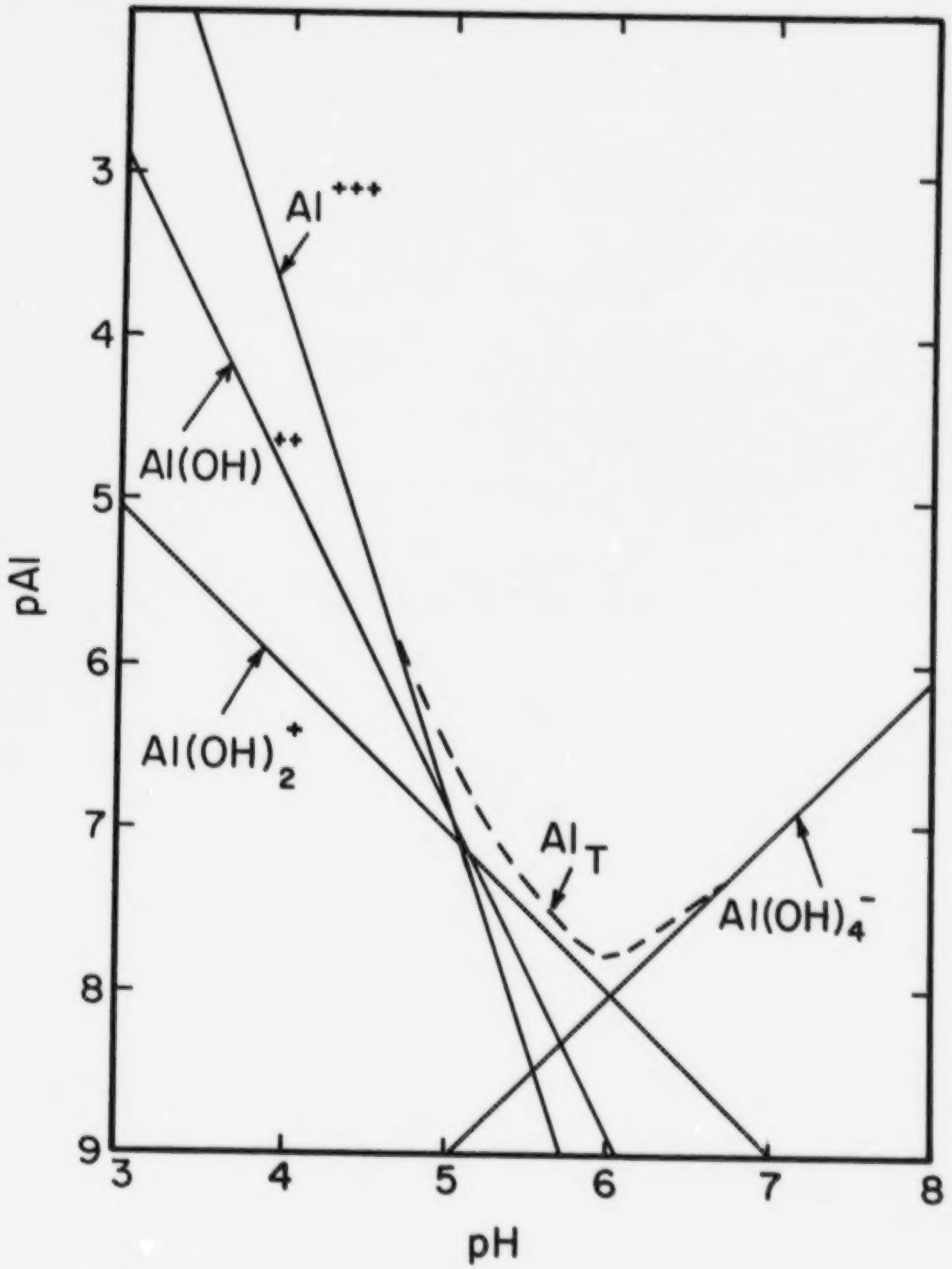
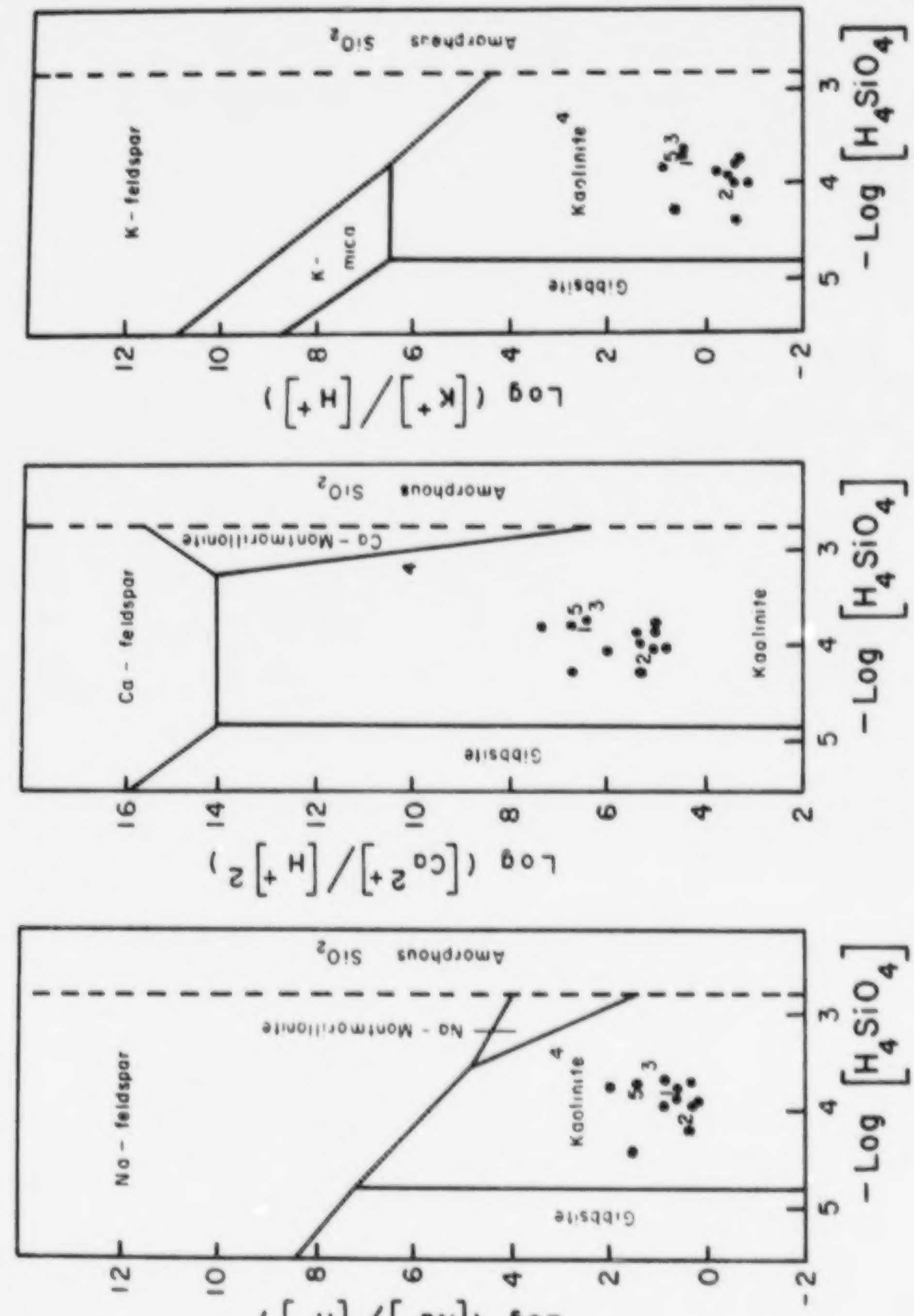


Fig.5-2


K - feldspar
K - mica
Kaolinite
Gibbsite
Amorphous SiO$_2$
Log ([K$^+$]/[H$^+$])
-Log [H$_4$SiO$_4$]
Ca - feldspar
Ca - Montmorillonite
Kaolinite
Gibbsite
Amorphous SiO$_2$
Log ([Ca^{2+}]/[H$^+$]2)
-Log [H$_4$SiO$_4$]
Na - feldspar
Na - Montmorillonite
Kaolinite
Gibbsite
Amorphous SiO$_2$
Log ([Na$^+$]/[H$^+$])
-Log [H$_4$SiO$_4$]
1
2
3
4
5
12
10
8
6
4
2
0
-2
16
14

CHAPTER 6

EXPERIMENTAL NEUTRALIZATION OF LAKES NEAR SUDBURY, ONTARIO

N.D. Yan and P.J. Dillon

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A. Introduction

The addition of basic calcium compounds, especially calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$), has long been practised as a means of increasing fish production in coloured, acidic ponds and lakes (Ness 1948). In addition to increases in pH and alkalinity, many other changes have been ascribed to these additions. Hasler et al. (1951) noted that the transparency of coloured lakes increased after additions of base resulting in deepened euphotic zones. Stross and Hasler (1960) reported decreases in concentration of total phosphorus, but increases have more commonly been observed. These increases, and increased alkalinity have been considered to be the cause of increased rates of phytoplankton production (Waters 1956, Hasler et al. 1951). Increased production of zooplankton (Stross et al. 1961) and benthic invertebrates (Bowling and Busbee 1961) have also been linked to additions of base to coloured (dystrophic) lakes.

Changes in chemistry and biota following additions of base may be different in coloured and clear acidic lakes. For example, oxygen concentrations decreased in the bottom waters of coloured Lake Flosak in Poland after additions of base (Hillbricht-Ilkowska 1977), whereas Wilander and Ahl (1975) reported no change attributable to base additions in the oxygen regimes of Lake Ljustjarn, a clear lake in Sweden. No change occurred in total nitrogen or total phosphorus concentrations following base additions to Lake Ljustjarn. However, Hillbricht-Ilkowska et al. (1977) reported that inorganic P and N levels increased the first year after base additions to Lake Flosak. They decreased below pre-treatment levels in subsequent years indicating, additionally, that the immediate changes in lake chemistry that follow base additions may be short lived.

Despite the paucity of information on the effects of base additions on the biota of acidic, clearwater lakes, basic substances are currently being added to a great number of lakes. Between 1977 and 1979, base was added to 700 acidic lakes and rivers in Sweden (Bengtsson et al. 1980). The status of existing and stocked fisheries has improved following these additions (Bengtsson et al. 1980, Hultberg and Grahn 1975).

In this chapter the results of neutralization experiments performed on acidic lakes in the Sudbury area are reviewed. These lakes have elevated levels of Cu and Ni and, thus, are different from experimentally neutralized lakes in Sweden. The overall purpose of the work was to determine the effects of an increase in pH on the chemistry and biota of acidic lakes in the Sudbury area. The findings may be used to assess the impact of a reduction in the input rates of strong acids to the lakes.

Neutralization experiments performed in Lohi, Middle and Hannah Lakes have been previously discussed in Adamski and Michalski (1975), Michalski and Adamski (1975), Scheider et al. (1975, 1976a), Scheider and Dillon (1976), Dillon et al. (1977, 1979) and Yan et al. (1979). Scheider et al. (1976b), Yan et al. (1977a, b) and Powell (1976) discussed the effects of additions of base on a fourth lake, Nelson Lake. Clearwater Lake (described in Chapter 1) was used as a reference for the neutralization experiments. Changes in plankton following neutralization were compared to acidic Swan Lake and non-acidic Joe Lake in addition to Clearwater Lake. Previously published information and recent unpublished information, especially from Lohi Lake, are summarized in this chapter.

B. Neutralization Technique

The criteria for selection of neutralizing agents were outlined by Scheider et al. (1975) and have been discussed by Grahn and Hultberg (1975). Calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) are inexpensive, are relative easy to handle, mobilized less metals from lake sediments in laboratory experiments than did other chemicals (Scheider et al. 1975), and provide only chemical species that are naturally significant components of lake waters.

Scheider et al. (1975) described the method used for addition of the neutralizing chemicals to the lakes. Briefly, epilimnetic water was pumped into a slurrying chamber in a moving boat where it was combined with dry chemicals supplied via a hopper. The mixture was discharged into the backwash of the boat which traversed the lake. Approximately 8 mt of dry chemical could be added per day.

Enough $Ca(OH)_2$ was added to Lohi and Middle lakes to raise the pH to ~8.0 (determined by titration), a level that was considered adequate for subsequent neutralization of the entire water column and of the top few cm of lake sediments (Scheider et al. 1975). Calcium carbonate was simultaneously added to Middle Lake with the intent of providing a residual buffering system. The amount of both chemical compounds added to Hannah Lake per unit volume was identical to that added to Middle Lake, while the required dosages for Nelson Lake were estimated by separate titration of Nelson Lake water.The quantities of base added to the study lakes are given in Table 6-1. A detailed schedule of additions is given in Appendix 1.

The kinetics of the reaction of calcium carbonate with strong

Table 6-1. Additions of $Ca(OH)_2$ and $CaCO_3$ to study lakes. Figures are nominal additions in 10^3 kg. Figures in parentheses are calculated additions of acid neutralizing capacity (ANC, μeq L^{-1}), correcting for assay of the neutralizing agent ($Ca(OH)_2$ - 48.7%Ca; $CaCO_3$ - 38.0%Ca) and assuming that the Mg content of the agents ($Ca(OH)_2$ - 3.37%Mg, $CaCO_3$ - 3.40%Mg) supplies ANC.

	1973			1974			1975			1976			Total		
	$Ca(OH)_2$		$CaCO_3$	$Ca(OH)_2$		$CaCO_3$	$Ca(OH)_2$		$CaCO_3$	$Ca(OH)_2$		$CaCO_3$	$Ca(OH)_2$		$CaCO_3$
Middle	20.0	(477)	13.6	-		-	-		-	-		-	20.0	(477)	13.6
Lohi	18.2	(196)	-	4.1	(45)	-	5.0	(184)	15.0	-		-	27.3	(426)	15.0
Hannah	-		-	-		-	13.0	(477)	7.5	-		-	13.0	(477)	7.5
Nelson	-		-	-		-	50.0	(58)	33.0	18.0	(24)	18.0	68.0	(82)	51.0

acid has been described in detail by Pearson and McDonnell (1974, 1975). Three reactions control the equilibration of $CaCO_3$ with acid:

1) Dissolution

$$CaCO_3(s) + H^+ \rightleftarrows Ca^{2+} + HCO_3^- \qquad (6\text{-}1)$$

2) Solution equilibration

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3 \qquad (6\text{-}2)$$

3) CO_2 Exsolution

$$H_2CO_3 \rightleftarrows H_2O + CO_2\,(g) \qquad (6\text{-}3)$$

The first reaction controls the rate of neutralization at low pH (<5), while the third reaction becomes rate-limiting at higher pH's.

The mechanism of neutralization by calcium hydroxide is completely different. The initial reaction of $Ca(OH)_2$ with strong acid occurs very rapidly since dissolution is almost instantaneous:

$$Ca(OH)_2(s) + H^+ \rightleftarrows Ca(OH)^+ + H_2O \qquad (6\text{-}4)$$

$$Ca(OH)^+ + H^+ \rightleftarrows Ca^{2+} + H_2O \qquad (6\text{-}5)$$

Depending on the amount of $Ca(OH)_2$ added, the pH may initially rise well above 7 because the rate of $Ca(OH)_2$ dissolution exceeds the rate of CO_2 diffusion from the atmosphere into the lake water. As CO_2 enters the lake, HCO_3^- (and CO_3^{2-}) are formed, producing H^+, and the pH drops until an equilibrium is reached as follows:

$$CO_2\ (gas) \rightleftarrows CO_2(aq) \qquad (6\text{-}6)$$

$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3 \qquad (6\text{-}7)$$

$$OH^- + H_2CO_3 \rightleftarrows H_2O + HCO_3^- \qquad (6\text{-}8)$$

In the study lakes (as well as in other acidic lakes), concentrations of several metals, notably Al, Mn, Cu, Ni, Zn and Fe were elevated prior to neutralization. At low pH (4-5), many of these metals contribute to the lake's base neutralizing capacity (BNC). The pH alone is, therefore, a poor measure of the lakes' total acidity. Reactions of added base with these metals are discussed subsequently.

C. Results

i. Major Ions

a. Middle and Hannah Lakes

The treatments of and effects of base additions on Middle and Hannah Lakes were very similar and are treated together in the following section.

The addition of $Ca(OH)_2$ and $CaCO_3$ raised the pH of Middle Lake from 4.4 to ~7 (Fig. 6-1), although a pH (whole-lake) as high as 8.76 was recorded immediately after treatment. The pH fell to 7.6 within a week, primarily due to atmospheric CO_2 invasion and/or possibly the slow reaction of the lake sediments with overlying water. The pH of Hannah Lake rose from 4.3 to ~7.0 following treatment. Values greater than 8 were not observed; however, there was no sampling for several days following the additions. In both of these lakes, pH has remained relatively stable, with means for the ice-free period ranging from 6.4-7.0 in Middle lake between 1974 and 1979, and from 6.6-7.1 in Hannah Lake between 1975 and 1979 (Table 6-2). An explanation for the stability of the pH in these 2 lakes is provided in Chapter 8.

The Mg^{2+}, K^{+} and SO_4^{2-} concentrations (Appendix 6) in Middle and Hannah Lakes did not change as a result of neutralization. Although the Mg^{2+} content of the neutralizing agents should have raised the concentration in each lake by 0.64 mg L^{-1}, the analytical precision was such that these changes were not detected.

The Na^{+} and Cl^{-} concentrations in both lakes have increased substantially during the course of this study. These changes are not related to neutralization, but to the use of NaCl and $CaCl_2$ for ice and dust control, respectively, on roads in the watersheds of the lakes. In Middle Lake, changes did not occur until 1975, a year and a half after chemical treatment (Fig. 6-2). In Hannah Lake, the increases also were apparent in 1975, but they coincided with snowmelt and spring runoff which occurred 2 months prior to additions of base. The Na^{+} and Cl^{-} changes were usually not equal, with the Cl^{-} increases exceeding the Na^{+} increases. The use of small quantities of $CaCl_2$ as well as larger amounts of NaCl in road maintenance in the Middle and Hannah Lakes watersheds is documented (S. Wilson, Ministry of Transportation and Communications pers. comm.). As indicated in Fig. 6-2, it is apparent that addition of these chemicals to the roads has had a major impact on the ionic balance of these study lakes. The

Table 6-2. Mean (for ice-free period) of pH, alkalinity (fixed endpoint measurements corrected; see Appendix 1) and calcium concentrations of experimentally neutralized lakes. Types of treatment applied are indicated with P = phosphorus additions. (Nelson 1 = main basin of Nelson Lake, Nelson 4 = NW basin).

Lake	Year	Treatment	pH	Alkalinity ($mg\ L^{-1}$ as $CaCO_3$)	Ca ($mg\ L^{-1}$)
Middle	1973[1]	$Ca(OH)_2+CaCO_3$	4.40	0[3]	9.8
	1974	-	7.01	5.7	14.2
	1975	P	6.56	2.6	12.5
	1976	P	6.41	2.1	12.6
	1977	P	6.37	1.9	12.0
	1978	P	6.65	3.7	11.5
	1979	-	6.54	3.9	10.9
Hannah	1973	-	4.31	0[3]	12.5
	1974	-	4.29	0[3]	11.4
	1975[2]	$Ca(OH)_2+CaCO_3$	7.02	5.7	20.1
	1976	P	6.67	3.4	19.2
	1977	P	6.59	3.7	18.1
	1978	P	6.96	5.1	16.5
	1979	-	7.07	7.5	15.1
Lohi	1973[1]	$Ca(OH)_2$	4.39	0[3]	6.2
	1974	$Ca(OH)_2$	6.04	0.7	7.9
	1975	$Ca(OH)_2+CaCO_3$	6.09	3.5	8.6
	1976	-	6.09	0.6	8.0
	1977	-	5.27	-0.5	7.2
	1978	-	4.79	-0.4	6.7
	1979	-	4.74	-0.8	6.6
Nelson-1	1975[1]	$Ca(OH)_2+CaCO_3$	5.73	0.4	4.1
	1976	$Ca(OH)_2+CaCO_3$	6.35	2.1	5.3
	1977	-	6.34	1.6	5.0
	1978	-	6.51	2.4	4.7
	1979	-	6.31	1.9	4.7
Nelson-4	1975	-	5.73	0.8	4.2
	1976[2]	$Ca(OH)_2+CaCO_3$	6.14	2.1	5.1
	1977	-	6.02	1.6	4.9

---

[1] pre-treatment data only

[2] post-treatment data only

[3] less than 0, but not measured, estimated inflection point alkalinities prior to additions of base were - 2.5, -3.0 and -2.0 mgL^{1} $CaCO_3$ for, Lohi, Hannah and Middle Lakes, respectively (See Chapter 8).

implications of this extra input of Ca^{2+} are discussed in Chapter 8.

Because the behaviour of Ca^{2+} approximates that of a conservative substance (see Chapter 8), the Ca^{2+} concentration in the lakewater immediately before and after the neutralization treatments can be used to indicate the fraction of the added $Ca(OH)_2$ and $CaCO_3$ that was in solution. In Middle Lake, the Ca^{2+} concentration rose from 9.8 mg L^{-1} prior to additions, to 18.0 mg L^{-1} immediately after additions, an increase consistent with complete dissolution of the added neutralizing agents (measured change of 8.2 vs. 8.5 mg L^{-1} added), since these figures are within the limits of analytical precision. However, slightly higher levels measured at 1 m above the sediment surface (20-22 mg L^{-1}) for a period of several months after additions indicate that a small amount of the added chemicals settled to the sediments and dissolved at the sediment-water interface.

The treatment of Hannah Lake increased the Ca^{2+} concentration from 12.8 to 21 mg L^{-1} immediately after additions, again an increase (8.2 mg L^{-1}) that was very similar to the increase expected on the basis of complete dissolution of neutralizing agents (8.5 mg L^{-1}). No separate measurements of the near-bottom waters of the lake were made. Because the neutralizing agents went into solution completely, the rate of change of the Ca^{2+} concentration in subsequent years indicates the natural rate of washout of materials in the lake (provided that a correction for $CaCl_2$ additions from road applications is applied). This is discussed more fully in Chapter 8.

Immediately following the additions of $Ca(OH)_2$ and $CaCO_3$ to Middle and Hannah Lakes, and concurrent with the increase in pH the alkalinity increased from ~-60 to +120 μeq L^{-1} in each lake, indicating that more than enough acid neutralizing capacity (ANC) was supplied to each lake to react with the acids present before treatment and to leave residual alkalinity. Subsequent changes in alkalinity resulting from the continuing input of strong acids and acidifying substances, from the natural washout of the residual ANC, and from whole-lake fertilization experiments (Chapter 7) are described in Chapter 8.

b. Lohi Lake

The first treatment of Lohi Lake, with $Ca(OH)_2$ only in 1973 (Table 6-1) raised the pH from 4.4 to ~ 7.0 (Fig. 6-1). However, the pH declined rapidly, and was only 5.5 by mid-summer, 1974. A subsequent treatment using $Ca(OH)_2$ in 1974 raised the pH to 6.5, but it again fell to ~ 5.5 by the spring of 1975. The third and final treatment with $Ca(OH)_2$ and $CaCO_3$ in 1975 elevated the pH to 6.7. The subsequent decline from 1975 to 1979 was more gradual than the earlier declines, but Lohi Lake effectively re-acidified (no ANC remained) by the spring of 1977. At that time the pH of the lake was ~ 5.4, and it continued to drop until it reached ~ 4.7 by the fall of 1979. A steady state pH will eventually be reached which reflects the input to and losses of acid from the lake.

The lack of success of the treatment of Lohi Lake compared to Middle and Hannah Lakes is a result of 3 factors. First, the sum of the 3 treatments of Lohi Lake provided less ANC (426 μeq L^{-1}, Table 6-1) than the single treatments of Middle and Hannah Lakes (477 μeq L^{-1}). This difference is reflected in the alkalinities measured in Lohi Lake following the treatments, since this alkalinity represents the excess ANC supplied above that needed to react with the acids present before treatment. Following the first treatment, the lake's alkalinity was 40-50 μeq L^{-1}. After the second it was 20 μeq L^{-1}, and following the third it was 80 μeq L^{-1}. All values were less than the 120 μeq L^{-1} remaining in Middle and Hannah Lakes after treatment.

Second, the flushing rate of Lohi Lake is greater than Middle or Hannah Lakes (see Table 15, Chapter 4). Therefore, the residual ANC is lost via the outflow more rapidly and strong acid is supplied more rapidly to the lake.

Third, the addition of nutrients following the neutralization of Middle and Hannah Lakes resulted in generation of substantial amounts of bicarbonate (a component of ANC) as a consequence of NO_3^- uptake by the phytoplankton. Primary production in Lohi Lake generated less ANC (discussed more fully in Chapter 8).

The Mg^{2+}, K^+, SO_4^{2-} and Na^+ concentrations in Lohi Lake did not change following any of the treatments. The Cl^- concentration, on the other hand, increased every year (Fig. 6-3) after measurements began in 1974. The lack of change in Na^+ concentration coupled with the knowledge that $CaCl_2$ was used on unsurfaced roads in the watersheds of Lohi and Clearwater Lakes for dust control (Ministry of Transportation and Communications) indicates that dissolution of this chemical is the source of the additional Cl^-. A similar increase was also measured in Clearwater Lake. This result also indicates that Ca^{2+} in excess of that in the $Ca(OH)_2$ and $CaCO_3$ from the treatments has been supplied to Lohi Lake. In consequence, use of the rate of decline of Ca^{2+} concentration in Lohi Lake as a measure of washout will be incorrect unless corrected for this excess Ca^{2+}.

The increases in Ca^{2+} concentration measured following the 3 treatments of Lohi Lake were 3.5, 0.6 and 2.2 mg L^{-1}. The first and second treatments supplied 3.5 and 0.8 mg Ca^{2+} L^{-1}, respectively, while the third supplied 3.25 mg Ca^{2+} L^{-1} to the Lake, indicating that in the last treatment, some added $CaCO_3$ may have settled to the lake bottom, from where it would have dissolved gradually into the overlying waters.

c. Nelson Lake

The treatment of Nelson Lake with a mixture of $Ca(OH)_2$ and $CaCO_3$ (58 μeq L^{-1}) in 1975 raised the pH from 5.7 to 6.5 in the main basin (station 1). The pH of the northwest basin (station 4) rose to 6.1 (Fig. 6-4) after a small addition of base in 1976. A second small addition of 24 μeq L^{-1} to the main basin of $Ca(OH)_2$ + $CaCO_3$ increased the pH for a short period of time. The pH has remained at ≈6.3 to the end of 1979, because the input of strong acids is not great relative to the lake volume (Chapter 8) and because some portions of the Nelson Lake watershed continue to supply alkalinity to the lake (see Chapter 5). Re-acidification of Nelson Lake should, therefore, be slow.

The increase in alkalinity after treatment was 40 μeq L^{-1} in Nelson Lake. By the end of 1979, there had been no noticeable decline. The Mg^{2+}, K^+, SO_4^{2-}, Na^+ and Cl^- concentrations did not change as a result of the treatments. The measured change in Ca^{2+} concentration of 1.0 mg L^{-1} in 1975 was identical to that expected, while the expected 1976 change (0.4 mg L^{-1}) was less than the analytical precision available at the time. There were no road applications of NaCl or $CaCl_2$ affecting Nelson Lake.

ii. Trace Metals

The annual average metal concentrations during the ice-free period are given for Clearwater, Lohi, Middle, Hannah and Nelson Lakes in Table 6-3. In Clearwater Lake, which was not chemically

Table 6-3. Summary of ice-free period averages of metal concentrations ($\mu g\ L^{-1}$) in SES lakes. Data for 1973 are from 1 m above bottom samples, 1974 are from 1 m below surface samples and for 1975-1979 are from composite samples. Pre-treatment only are presented for 1973 from Middle and Lohi Lakes and for 1975 from Nelson Lake (Station 1). Post-treatment data only are presented for 1975 from Hannah Lake.

Lake	Metal	Concentration						
		1973	1974	1975	1976	1977	1978	1979
Clearwater	Cu	98	101	100	91	81	74	60
	Ni	283	289	272	271	278	257	220
	Zn	48	47	49	55	39	37	31
	Al	420[1]	516	447	397	381	324	272
	Fe	114	94	132	94	88	57	55
	Mn	328	310	289	301	290	297	282
Lohi	Cu	84	44	43	37	44	71	64
	Ni	254	195	166	176	221	237	210
	Zn	42	32	28	38	33	32	29
	Al	-	143	106	123	97	157	140
	Fe	90[2]	51	114	93	72	58	43
	Mn	284	243	174	140	168	279	290
Middle	Cu	496	66	117	68	60	43	25
	Ni	1060	349	499	462	427	354	287
	Zn	91	28	41	41	29	23	17
	Al	-	206	123	78	53	37	24
	Fe	143	121	93	175	106	111	92
	Mn	354	161	211	219	236	190	170
Hannah	Cu	1090	1110	58	52	41	45	25
	Ni	1620	1870	346	427	393	307	233
	Zn	123	120	32	35	21	16	8
	Al	-	1100	93	66	64	43	26
	Fe	57	47	90	71	169	76	152
	Mn	398	340	188	154	116	73	66
Nelson	Cu	-	-	22	15	4	3	2
	Ni	-	-	17	11	7	7	7
	Zn	-	-	18	14	6	4	4
	Al	-	-	87	30	21	17	19
	Fe	-	-	61	31	19	20	20
	Mn	-	-	63	28	13	18	14

---

[1] one value only

[2] one value only from whole lake composite sample. Average of 1 m above bottom samples was 320 $\mu g\ L^{-1}$ but because these waters were anoxic for a large fraction of the time, these values did not reflect lake concentrations.

treated, there was a slight decrease in Cu concentrations between 1973 and 1977. Decreases in concentration of several metals in 1978 and 1979 reflect the shutdown of the Copper Cliff smelter and the subsequent reduced input of metals from precipitation (Chapter 2).

The changes in concentrations of metals that resulted from the addition of neutralizing agents are given in Table 6-4. Additions of base produced significant reductions in concentrations of Cu, Ni, Mn, Al and Zn in Middle, Hannah, Lohi and Nelson Lakes. Fe was significantly reduced in all but Hannah Lake. These reductions in metal concentrations were the result of reduced metal solubility at higher pH and/or physical removal by settling of the particulate metal component (eg. as phytoplankton, zooplankton, etc.). As the concentrations remained low in the years following additions of base despite continued high loadings to the lakes (Chapter 2) the former mechanism must have been very important. In Nelson Lake, additional decreases in metal concentrations were observed in 1977, the year following the second treatment. This probably resulted from mixing of the epilimnetic water of higher pH with the hypolimnion during the fall overturn of 1976, resulting in precipitation of metals that had been in the hypolimnion.

Further evidence that metal concentrations were controlled by pH was provided by changes in metal concentrations that occurred in Lohi Lake from 1977 to 1979 after the lake reacidified. Copper, Ni, Al, Zn and Mn concentrations remained as low or lower than post-treatment levels until 1976, then increased as the lake's pH declined (Table 6-3). The ratio of metal levels in Lohi and Clearwater Lakes are plotted against time in Fig. 6-5. From these plots it is evident that Cu, Ni, Mn and Zn levels in Lohi Lake had returned to pretreatment levels by 1978. Inadequate Al and Fe

Table 6-4. Percentage decrease in average metal concentrations after experimental additions of base.

Lake	Years Compared		Decrease (%)					
	Pre-Treatment	Post-Treatment	Cu	Ni	Zn	Fe	Mn	Al
Middle	1973	1974	87	67	69	15	54	-
Hannah	1974	1975	95	81	73	89	45	91
Lohi	1973	1974	48	23	24	43[1]	15	-
Nelson	1975	1976	32	35	22	49	56	66
		1977	82	59	67	69	79	75

[1] using 90 µg L^{-1} as concentration for 1973

pretreatment data in 1973 preclude any consideration of the effects of reacidification on the concentration of these metals.

iii. Quantitative Considerations Regarding the Application of Neutralizing Reagents

There are a number of components of total acidity of lake waters other than free hydrogen ion that must be neutralized by base additions before a reserve of ANC can be established. These components include the acidic metals (principally Al) and the organic and inorganic carbon pool. In addition, reaction with the lake sediments may consume some of the added base. It is, of course, desirable that ANC in excess of that required to react with the acidity be added so that residual ANC will remain and the pH will be maintained in the 6.0-7.5 range. If insufficient base is added, the pH may rapidly rise and the mineral and carbonate acidity decline, but as the Al is hydrolyzed, the pH will drop (Driscoll 1980). These hydrolyzed species of Al may be extremely toxic to fish (Baker and Schofield 1980).

In the neutralized study lakes (Middle, Hannah, Lohi, Nelson) the total organic carbon (TOC) concentrations were very low before and after treatment (pre-treatment levels estimated from Hannah Lake 1975 data and Clearwater Lake 1975-79 data). The base neutralizing capacity (BNC) of the organic carbon pool was, therefore, low. In Middle, Hannah and Lohi Lakes, there was a great drop in total Al concentration following the neutralization treatment although pretreatment levels could only be estimated in Middle and Lohi Lakes. The pH of minimum $Al(OH)_3$ solubility is about 6.0 (Fig. 6-6) which is consistent with the decrease in total Al concentration. Based on a simple chemical model of gibbsite, at a pH of 4.3 there is 4-fold more Al^{3+} than $Al(OH)^{2+}$. At pH >6,

$Al(OH)_4^-$ becomes important and total Al in solution may again rise. As a first approximation, subsequent calculations (Tables 6-5 to 6-8) assume that 3 moles of base were consumed by each mole of Al lost, and that the remaining Al was associated with 2 moles of base per mole.

$$Al^{3+} + 3\ OH^- \rightarrow Al\ (OH)_3(s) \qquad (6\text{-}9)$$

$$Al(OH)^{2+} + 2\ OH^- \rightarrow Al\ (OH)_3(s) \qquad (6\text{-}10)$$

There was also a substantial decline in Cu and Ni concentrations in all study lakes. Spear and Pierce (1979) have shown that at pH of 4.0 - 4.5 almost all of the Cu exists as the Cu^{2+} species, but at pH 7, $CuCO_3^0$ becomes the most important species in solution, followed by Cu^{2+}, $Cu(OH)^+$ and $Cu(CO_3)_2^{2-}$ (Fig. 6-7). Therefore, both the Cu lost from the study lakes as well as that remaining in solution following the increase in pH are assumed to be associated with an equivalent consumption of base. Note that the speciation is approximate only since it depends on C_T (total inorganic carbon) which, in the study lakes, is at least an order of magnitude lower than 10^{-3}M, the lowest level shown in Fig. 6-7. In the following calculations, it is also assumed that at pH 4.0-4.5, the Ni exists primarily as Ni^{2+}, and that this consumes an equivalent amount of base as the pH reaches 7.

The lakes' sediments contained significant base neutralizing capacity (BNC) as documented by titration (Adamski and Michalski, 1975). This is also demonstrated by changes in the pH profiles

Table 6-5. Quantitative breakdown of components or reactions using acid neutralizing capacity (ANC) in Middle Lake following addition of base in 1973.

Component or reaction using ANC	Concentration change	ANC required ($\mu eq\ L^{-1}$)
H^+	pH=4.40 → pH=8.76	40
TOC	~1mg L^{-1}	~1[1]
Al^{3+}	(1100 $\mu g\ L^{-1}$ → 206 $\mu g\ L^{-1}$)[3]	114
Cu^{2+}	496 $\mu g\ L^{-1}$	16
Ni^{2+}	1060 $\mu g\ L^{-1}$	36
Other metals (Fe, Mn, Zn)		~5
Alkalinity generated		104[2]
	Total	316
	ANC added	477
Reactions with sediments and additional components		161

---

[1] estimated from Driscoll (1980)

[2] 7.3 mg $CaCO_3\ L^{-1}$ as TFA, corrected to a TIA of 116 $\mu eq\ L^{-1}$ and reduced by the HCO_3^- produced from H_2CO_3

[3] initial Al concentration estimated from Hannah Lake data since no measurements were made prior to addition of base; final Al concentration taken from 1974 data

Table 6-6. Quantitative breakdown of components or reactions using ANC in Lohi Lake following first addition of base, in 1973.

Component or reaction using ANC	Concentration change	ANC required ($\mu eq\ L^{-1}$)
H^+	pH=4.4 → pH=7.0	40
TOC	~1 mg L^{-1}	~1[1]
Al^{3+}	(480 µg L^{-1} → 175 µg L^{-1})[3]	47
Cu^{2+}	90 µg L^{-1}	3
Ni^{2+}	250 µg L^{-1}	8
Other metals (Fe, Mn, Zn)		~5
Alkalinity generated		6[2]
	Total	110
	ANC added	196
Reactions with sediments and additional components		86

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[1] estimated from Driscoll (1980)

[2] 2.4 mg $CaCO_3$ L^{-1} as TFA, corrected to a TIA of 18 µeq L^{-1} and reduced by the HCO_3^- produced from H_2CO_3

[3] initial concentration estimated on the basis of the [Al] in Clearwater Lake (1974), final concentration estimated from Lohi Lake, 1974

Table 6-7. Quantitative breakdown of components or reactions using ANC in Hannah Lake following addition of base in 1975.

Component or reaction using ANC	Concentration change	ANC required (μeq L^{-1})
H^+	pH=4.64 → pH=7.0	23
TOC	~1 mg L^{-1}	~1[1]
Al^{3+}	1100 μg L^{-1} → 90 μg L^{-1}	119
Cu^{2+}	910 μg L^{-1}	29
Ni^{2+}	1350 μg L^{-1}	46
Other metals (Fe, Mn, Zn)		~7
Alkalinity generated		104[2]
	Total	329
	ANC added	477
Reactions with sediments and additional components		148

[1] estimated from Driscoll (1980)

[2] 7.3 mg $CaCO_3$ L^{-1} as TFA, corrected to a TIA of 116 μeq L^{-1} and reduced by the HCO_3^- produced from H_2CO_3

Table 6-8. Quantitative breakdown of components or reactions using ANC in Nelson Lake following first addition of base, in 1975.

Component or reaction using ANC	Concentration change	ANC required (μeq L^{-1})
H^+	pH=5.73 → pH=6.53	2
TOC	~1 mg L^{-1}	~1[1]
Al^{3+}	87 μg L^{-1} → 55 μg L^{-1}	8
Cu^{2+}	22 μg L^{-1}	1
Ni^{2+}	17.1 μg L^{-1}	1
Other metals (Fe, Mn, Zn)		-
Alkalinity generated		14[2]
	Total	27
	ANC added	82
Reactions with sediments and additional components		55

[1] estimated from Driscoll (1980)

[2] change in alkalinity of 26 μeq L^{-1}, corrected for HCO_3^- production from H_2CO_3

following chemical treatment. Walsh (1977, Fig. A4-2) and Scheider et al. (1975) showed that at least the upper 2 cm of the sediments of untreated Clearwater Lake were acid (pH 4.3-5.2), while the deeper sediments had pH values between 5.5 and 6.0. The upper 6-8 cm of sediment at 3 stations in Hannah Lake were acid in 1974 before treatment (Fig. 6-8), while after additions of base the surficial sediments were neutralized (Fig. A4-2, Fig. 6-9). In Middle and Lohi Lakes there was a significant increase in pH of the surface layer of sediment following chemical treatment (Scheider et al. 1975). The surficial sediment pH had risen to 5.8-7.1 at most stations (Fig. A4-2); however, single cores taken in 1978 (Fig. 6-9) showed a decline in pH in the topmost layers, suggesting that the sediments might have been continuously losing ANC to the water column.

Summaries of the calculated amounts of ANC consumed by various components are given in Tables 6-5 to 6-8. In general, the largest proportions of added base were used to hydrolyze the Al, neutralize the upper sediments, and supply residual alkalinity. Lesser amounts neutralized the free H^+ and reacted with Cu, Ni and perhaps other metals. The minor contribution of Cu and Ni to the consumption of ANC indicated that any uncertainty in the speciation of these metals (noted earlier) was of little consequence. Hence, the total acidity of the lakes was much greater than the free acidity indicated by the pH.

iv. Nutrients

Previous investigators have disagreed on the effects of base additions on concentrations of TP. If additions of base produced changes in concentrations of TP in Middle, Lohi, Hannah or Nelson

Lakes, the changes were smaller than the year to year variations of TP observed in untreated Clearwater Lake (Table 6-9). This supports the conclusion of Wilander and Ahl (1975) that neutralization of clear, acidic lakes does not result in changes in concentrations of TP.

In Lohi, Middle and Hannah Lakes, neutralization was accompanied by a small increase in concentrations of Si (Table 6-9). Reasons for this increase are unknown but they were not related to changes in relative abundances of diatoms.

Neutralization did not result in any changes in concentrations of total nitrogen (TN=TIN+TON), but it may have resulted in changes in the speciation of nitrogen. Despite the large year to year changes in pH, TN in Lohi Lake did not vary more over the course of the study (Table 6-10) than did that of Clearwater Lake (220 ± 28 $\mu g\ L^{-1}$ vs. 193 ± 23 $\mu g\ L^{-1}$, mean ± 95% confidence interval, respectively). There was no apparent decline in TN in Middle, Hannah or Nelson Lakes following neutralization and prior to any fertilization experiments. However, the fractionation of the nitrogen between inorganic ($TIN = NO_3^- + NO_2^- + NH_4^+$) and organic forms may have been affected. In the years following the additions of base to Lohi Lake, the percent of the TN in the inorganic form dropped from 54% prior to the first treatment to a low of 27% in 1977. The distribution then reversed as Lohi Lake re-acidified, until 58% of the TN was in the inorganic form by 1979. However, in Clearwater Lake, the fraction of TN in inorganic form declined from 60% in 1973 to a low of 41% in 1975, then rose to 56-60% in 1977-79 making interpretation of changes in Lohi Lake difficult. The Lohi Lake data indicate that changes in the speciation of nitrogen following additions of base would be very

Table 6-9. Summary of average concentrations over the ice-free period of TP (µg L^{-1}) and Si (mg L^{-1}) in study lakes. Data from years of fertilization in Middle and Hannah Lakes are excluded.

Year	Clearwater		Lohi		Middle		Hannah		Nelson - 1	
	TP	Si	TP	Si	TP	Si	TP	Si	TP	Si
1973	5.9	2.0	6.1[1]	1.3[1]	7.3[1]	1.3[1]	8.4	0.51	-	-
1974	5.5	2.0	5.0	1.6	7.1	1.6	5.7	0.54	-	-
1975	4.1	2.1	3.7	2.2			3.0[2]	1.2[2]	4.6[1]	0.26[1]
1976	5.2	1.8	5.4	2.2					5.3	0.26
1977	6.5	1.6	7.3	2.2					7.9	0.22
1978	4.6	1.8	5.6	2.2					7.2	0.24
1979	2.4	1.6	5.7	0.77					3.8	0.72

[1] pre-treatment data only

[2] post-treatment data only

Table 6-10. Fractionation of nitrogen species in study lakes. Results are averages for the ice free period and are in µg L^{-1} except for the fraction of of total N in inorganic form (TIN/TN) which is in %.

Lake	Year	Treatment	pH	NH_4^+-N	TKN	NO_3^--N	TIN	TON	TIN/TN
Clearwater	1973	none	4.29	35	131	108	143	96	60
	1974	none	4.24	15	84	65	80	69	54
	1975	none	4.33	22	144	64	86	122	41
	1976	none	4.23	26	132	53	79	106	43
	1977	none	4.10	36	102	62	98	66	60
	1978	none	4.40	34	128	86	120	94	56
	1979	none	4.41	32	116	76	108	84	56
Lohi	1973[1]	$Ca(OH)_2$	4.39	69	193	77	146	124	54
	1974	$Ca(OH)_2$	6.04	24	145	77	101	121	45
	1975	$Ca(OH)_2+CaCO_3$	6.09	26	180	55	81	154	34
	1976	none	6.09	29	197	36	65	168	28
	1977	none	5.27	23	150	26	48	127	27
	1978	none	4.79	43	183	69	112	140	44
	1979	none	4.74	27	96	70	97	69	58
Middle	1973[1]	$Ca(OH)_2+CaCO_3$	4.40	38	180	442	480	142	77
	1974	none	7.01	48	183	417	465	135	78
	1975	P	6.56	28	270	298	326	242	57
	1976	P	6.41	61	368	83	143	307	32
	1977	P	6.37	65	311	94	159	246	39
	1978	P	6.65	49	320	29	78	271	22
	1979	none	6.54	63	247	34	97	184	35
Hannah	1973	none	4.31	25	224	658	683	199	77
	1974	none	4.29	17	150	576	593	133	82
	1975[2]	$Ca(OH)_2+CaCO_3$	7.02	66	183	524	590	117	83
	1976	P	6.67	64	329	297	361	265	58
	1977	P	6.59	64	362	147	211	298	41
	1978	P	6.96	51	349	92	143	298	32
	1979	none	7.07	44	296	51	95	252	28
Nelson	1975[1]	$Ca(OH)_2+CaCO_3$	5.73	19	178	21	40	159	20
	1976	$Ca(OH)_2+CaCO_3$	6.35	24	167	26	50	143	26
	1977	none	6.34	27	144	16	43	117	27
	1978	none	6.51	28	178	17	45	150	23
	1979	none	6.31	24	162	14	38	138	22

[1] Pre-treatment data only
[2] Post-treatment data only

gradual, on the order of years. Hence any changes in speciation of N in Middle and Hannah Lakes attributable to additions of base were obscured by the subsequent fertilization of the lakes. There was no change in the speciation of nitrogen in Nelson Lake following chemical treatment (Table 6-10).

v. Transparency

The addition of base had no effect on the Secchi transparency of Nelson Lake (Table 6-11). In Middle, Lohi and Hannah Lakes the immediate effects of neutralization on Secchi transparency were different from the long-term effects. Secchi transparency increased immediately after additions of base, at least partially because of major decreases in biomass of phytoplankton. In Lohi Lake, for example, the biomass prior to additions of base in 1973 was 0.65 mg L^{-1} and Secchi depth was 8.0 m. Immediately after additions of base, Secchi depth increased to 17 m, the highest level ever recorded in the lake, as phytoplankton biomass declined to 0.023 mg L^{-1}. Although not measured, decreases in dissolved organic matter may have also contributed to increased clarity.

In the long-term, in contrast, neutralization resulted in decreases in clarity. The average annual Secchi transparency in Middle and Hannah Lakes decreased after base additions (Table 6-11), but Scheider et al. (1975) indicated that some of the decline may have been attributable to increased turbidity resulting from road construction in the lakes' watersheds. No such construction occurred in the watershed of Lohi Lake at the times of base additions. Average annual Secchi transparency in Lohi Lake was significantly correlated with pH ($r = 0.93$). The transparency decreased when base was added to the lake and increased after the reacidification of the Lake in 1977 (Table 6-11). Decreases in

Table 6-11. pH, Secchi depth, phytoplankton biomass and chlorophyll a, for Lohi, Middle, Hannah and Nelson Lakes. Data are averages for the ice-free period.

Lake	Year	pH	Secchi (m)	Biomass (mg L^{-1})	Chlor a (mg m^{-3})
Lohi	1973[1]	4.39	8.8	0.65	1.7
	1974	6.04	5.6	0.44	0.9
	1975	6.09	5.7	0.25	1.3
	1976	6.09	5.7	0.24	1.3
	1977	5.27	6.9	0.32	1.2
	1978	4.79	9.3	0.13	0.7
	1979	4.74	7.6	0.57	0.8
Middle	1973[1]	4.40	10.5	0.46	0.91
	1974	7.01	2.9	0.16	0.92
Hannah	1973[3]	4.31	$\sim z_{max}$	0.26	0.78
	1974[3]	4.29	$\sim z_{max}$	0.34	0.68
	1975[2]	7.02	6.0	0.13	0.74
Nelson-1	1975[1]	5.73	8.5	0.27	1.0
	1976	6.35	8.2	0.48	1.3
	1977	6.34	7.8	0.43	1.4
	1978	6.51	8.3	0.37	1.6

[1] pre-treatment data only

[2] post-treatment data only

[3] in Hannah Lake in 1973, about 50% of the Secchi depths were $\geq z_{max}$. In 1974, 50% were also $\geq z_{max}$, but in 1975 all measurements were $< z_{max}$.

Secchi transparency in Lohi Lake and indeed in Middle Lake from 1973-1974 or Hannah Lake from 1974 to 1975 were not associated with increases in phytoplankton biomass or chlorophyll concentration. In fact, the reverse was observed (Table 6-11). This supports the observation of Almer _et al_. (1978) that increases in transparency in acidic lakes in Sweden are not associated with decreases in phytoplankton stocks, but are more likely the result of precipitation of dissolved, coloured organic matter by Al.

vi. Temperature and Oxygen

The thermal regimes of lakes are governed by a complex interaction of factors including physical factors such as morphometry, fetch, insolation, etc., and by chemical and biological factors such as concentration of dissolved and suspended organic and inorganic material which together govern lake transparency. Since both the historical acidification and subsequent neutralization and reacidification of Lohi Lake influenced the transparency of the (Table 6-11) changes in the thermal regime of the lake were to be anticipated.

The thickness of the epilimnion decreased when Lohi Lake was neutralized but increased again after the reacidification of the lake in 1977 (Table 6-12). The epilimnion was thinnest in 1975 and 1976 even though surface wind speeds were greater in these two years than in all other years of study (Table 6-13). The temperature and heating rate of the hypolimnion decreased when the lake pH was >6.0 and increased when the lake reacidified. Both were lowest in 1975 and 1976 even though surface irradiances, as estimated by numbers of hours of bright sunshine, were higher in these two years than in all other years of study (Table 6-13). Changes in epilimnetic thickness and hypolimnetic temperature and heating rate were

Table 6-12 Changes in average pH, Secchi depth, epilimnetic thickness (z_{epi}), hypolimnetic temperature (θ_{hypo}) and hypolimnetic heating rate in Lohi Lake. Ice-free seasons averages are presented, except where otherwise indicated.

Year	pH	Secchi Depth (m)	z_{epi}[1] (m)	θ_{hypo}[2] (°C)	Heating Rate[3] (°C day^{-1})
1973	4.4	8.8	10.2	12.6	0.045
1974	6.04	5.6	8.8	9.2	0.026
1975	6.09	5.7	7.3	7.4	0.016
1976	6.09	5.7	7.1	8.9	0.022
1977	5.27	6.9	9.6	8.9	0.032
1978	4.79	9.3	9.5	9.6	0.046
1979	4.74	7.6	10.0	10.6	0.049

[1] mean for July and August

[2] mean at 14m for June - September

[3] slope of a linear regression equation with θ_{hypo} as the dependent variable and time since establishment of the hypolimnion as the independent variable.

Table 6-13. Level of significance of t-tests of difference between years pairing months ($p<0.05$ only), for average wind speed and number of hours of bright sunshine, the latter in parenthesis. May to October data were used. Mean values are included. All data from Environment Canada, Meteorological Station at the Sudbury Airport.

Wind Speed ($km\ h^{-1}$)	Hours of Bright Sun ($month^{-1}$)	Year	Level of Significance					
			1974	1975	1976	1977	1978	1979
17.7	199	1973	-	.05	.05	-	-	.01
17.9	190	1974		(.05)	(.05)	-	-	.01
20.2	243	1975			-	-	-	.01
18.9	232	1976				-	-	.05
18.7	223	1977					-	.01
18.0	226	1978						.05
15.5	215	1979						

Table 6-12 Changes in average pH, Secchi depth, epilimnetic thickness (z_{epi}), hypolimnetic temperature (θ_{hypo}) and hypolimnetic heating rate in Lohi Lake. Ice-free seasons averages are presented, except where otherwise indicated.

Year	pH	Secchi Depth (m)	z_{epi}^{1} (m)	θ^{2}_{hypo} (°C)	Heating Rate[3] (°C day^{-1})
1973	4.4	8.8	10.2	12.6	0.045
1974	6.04	5.6	8.8	9.2	0.026
1975	6.09	5.7	7.3	7.4	0.016
1976	6.09	5.7	7.1	8.9	0.022
1977	5.27	6.9	9.6	8.9	0.032
1978	4.79	9.3	9.5	9.6	0.046
1979	4.74	7.6	10.0	10.6	0.049

[1] mean for July and August

[2] mean at 14m for June - September

[3] slope of a linear regression equation with θ_{hypo} as the dependent variable and time since establishment of the hypolimnion as the independent variable.

Table 6-13. Level of significance of t-tests of difference between years pairing months ($p<0.05$ only), for average wind speed and number of hours of bright sunshine, the latter in parenthesis. May to October data were used. Mean values are included. All data from Environment Canada, Meteorological Station at the Sudbury Airport.

Wind Speed (km h^{-1})	Hours of Bright Sun ($month^{-1}$)	Year	Level of Significance 1974	1975	1976	1977	1978	1979
17.7	199	1973	-	.05	.05	-	-	.01
17.9	190	1974		(.05)	(.05)	-	-	.01
20.2	243	1975			-	-	-	.01
18.9	232	1976				-	-	.05
18.7	223	1977					-	.01
18.0	226	1978						.05
15.5	215	1979						

undoubtedly reflections of the changes in the transparency of Lohi Lake which accompanied changes in lake pH.

Water clarity can indirectly affect oxygen regimes in lakes. Schindler et al. (1980) indicated that the experimental acidification of Lake 223 in northwestern Ontario increased lake transparency. In consequence, oxygen maxima related to localized photosynthetic activity occurred at greater depths than those observed prior to acidification. Similarly, depths at which oxygen maxima occurred in Lohi Lake were correlated with clarity. Maxima occurred at 12-13 m in 1977-1979, but at 9-11 m in 1975 and 1976 (Appendix 5) when transparencies were lower.

In Chapter 1 it was indicated that the oxygen deficit of the tropholytic zone was not lower in Clearwater Lake than in non-acidic Shield lakes. Depletion rates for Lohi Lake were calculated for 1976 and 1978. The depletion rate in 1976 was 0.016 mg O_2 $cm^{-2}day^{-1}$, a rate similar to that of Clearwater Lake. This suggests that neutralization of the lake had not increased rates of production of organic matter. In 1978, however, a low rate of 0.006 mg O_2 $cm^{-2}day^{-1}$ was calculated, indicating that acidification of lakes may be accompanied by a transient decline in primary productivity.

vii. Phytoplankton

a. Biomass

Prior to the additions of base, the biomass of the phytoplankton communities of Middle, Lohi and Hannah Lakes were 0.46, 0.65 and 0.26 - 0.34 mg L^{-1}, respectively, when averaged over the ice-free season (Table 6-14). Despite the low pH values and high concentrations of metals in these lakes, their biomasses were similar to those of the much less acidic Nelson and Joe Lakes

Table 6-14: Summary of selected data on phytoplankton and pH of the SES lakes. Only data prior additions of phosphorus are included. Data are averages for the ice-free period except where indicated. Prymnesiophyceae are included in chrysophyceae.

Lake	Year	pH	Number of genera per collection	Biomass (mg L^{-1})	Percent Biomass					
					Dino-phyceae	Crypto-phyceae	Chloro-phyceae	Chryso-phyceae	Cyano-phyceae	Bacillario-phyceae
Lohi	1973^1	4.39	6.8	0.65	32	24	43	2	0	<1
	1974	6.04	8.9	0.44	21	2	17	56	<1	4
	1975	6.09	9.9	0.21	25	7	20	47	<1	2
	1976	6.09	8.7	0.25	35	15	8	41	<1	1
	1977	5.27	12.1	0.31	67	13	4	15	<1	<1
	1978	4.79	9.9	0.14	28	8	36	28	<1	<1
	1979^3	4.74	12.2	0.23 (0.49)	8(4)	12(6)	37(17)	31(19)	<1(<1)	2(55)
Middle	1973^1	4.40	6.0	0.46	58	29	11	3	0	0
	1974	7.01	5.8	0.17	<1	<1	2	84	2	12
Hannah	1973	4.31	7.9	0.26	65	1	10	11	<1	13
	1974	4.29	9.1	0.34	21	<1	30	34	<1	14
	1975^2	7.02	9.7	0.12	<1	<1	4	66	8	21
Swan	1977	3.96	8.8	2.14	43	52	<1	4	<1	<1
Clearwater	1973-1978	4.27	9.1	0.49	45	17	23	12	<1	3
Joe	1976	5.57	18.0	0.34	2	8	7	13	<1	70
Nelson-1	1975^1	5.73	19.6	0.34	5	5	36	20	3	31
	1976	6.35	18.5	0.47	14	14	19	12	<1	41
	1977	6.34	16.3	0.43	9	4	4	10	<1	74
	1978	6.51	20.5	0.36	12	6	12	21	<1	50
-4	1975	5.73	18.3	0.34	4	2	29	14	24	27
	1976^2	6.14	19.6	0.77	6	13	13	10	<1	58
	1977	6.02	20.0	0.60	23	6	7	6	<1	58

[1] pre-base addition data only

[2] post-base addition data only

[3] excludes data from June 12, 1979 (peak of Rhizosolenia longiseta) for reasons stated in text; numbers in parentheses include data from June 12.

(Table 6-14) and to the mean biomass of 0.62 mg L^{-1} reported by Yan (1979) for 9 non-acidic, oligotrophic lakes in south-central Ontario.

Additions of base raised the pH of Middle, Lohi and Hannah Lakes from between 4.3 and 4.7 to ≈7.0 and were immediately followed by a drastic decline in standing stocks of phytoplankton. The reductions in 1973 in Lohi Lake are evident in Fig. 6-10. Biomass in Middle Lake was reduced to <0.025 mg L^{-1} immediately after additions of base in 1973. In Hannah Lake, the biomass was 0.7 mq L^{-1} prior to additions of base in the early spring of 1975 but did not exceed 0.1 mg L^{-1} for two months after additions of base. (Appendix 7). Smaller additions of base which resulted in smaller changes in pH such as in Lohi Lake in 1974 and in 1975 (Fig. 6-10) did not result in decreases in biomass.

In the main basin of Nelson Lake (Station 1), additions of base raised lake pH from 5.8 to 6.4 and produced no immediate or long term changes in phytoplankton biomass (Table 6-14). Hillbricht-Ilkowska et al. (1977) described experiments in which the pH of dystrophic Lake Flosak, in Poland, was raised from 5.5-6.0 to 7.0-8.0, a change similar to that of Nelson Lake. As in Nelson Lake, the phytoplankton biomass of Lake Flosak did not change significantly, being 3.8 mg L^{-1} in the control year and 2.7-7.4 mg L^{-1} in the four years after additions of base. Similarly, Hörnström (1979) concluded that the gradual elevation of the pH of Swedish Lake Ostra Nedsjon from 5.1 in 1970 to 5.8-7.0 from 1973 to 1977 produced no changes in biomass of the lake's phytoplankton.

In Middle, Hannah and Lohi Lakes, phytoplankton biomass recovered within a few months of additions of base, and average biomasses approached, but did not exceed pre-neutralization levels (Table 6-14). As phytoplankton biomass was correlated with concentrations of TP, not with pH prior to additions of base, (Chapter 1), and as additions of base did not change concentrations of TP this result was reasonable.

The pH of Lohi Lake fell from 6.1 in 1976 to 5.3 in 1977 and to <5.0 in 1978 and 1979. Phytoplankton biomass was slightly higher in 1977 (0.31 mg L^{-1}) than in any other year from 1975 to 1979 (Table 6-14). Although levels of Al were only ~100 μg L^{-1} these results do not support the hypothesis of Almer _et al_. (1978) that the availability of phosphorus, and therefore the biomass of phytoplankton, may be reduced in lakes of pH 5.0 to 6.0 because of complexation with Al. The lowest average phytoplankton biomass in Lohi Lake (0.14 mg L^{-1}) occurred in 1978, the year that lake pH first fell below 5.0. This suggests that although phytoplankton biomass is controlled by TP in acidic as in non-acidic lakes, there may be short-term reductions in biomass following acidification of lakes.

b. Community Composition

Prior to additions of base there were between 6.0 and 9.1 genera of phytoplankton per collection, on average, in Hannah, Middle and Lohi Lakes. This number is similar to that of the other study lakes with pH <5.0 (Swan and Clearwater), but only about one-half to one-third of the average number of genera observed in intermediately acidic Nelson and Joe Lakes (Table 6-14). Numbers of genera observed in Nelson and Joe Lakes were similar to numbers observed in non-acidic Precambrian Shield Lakes (Yan 1979).

The richness of genera (average number of genera per collection) did not change after additions of base to Nelson Lake

(Table 6-14). Hörnström (1979) noted that normal diversities were usually re-established in phytoplankton communities of Swedish acidic lakes within one or two years of additions of base. A component of diversity, normal richness of genera, (16-20 genera per collection in non-acidic Sudbury area lakes) was not re-established in Lohi during the three years (1974-1976) when lake pH remained above 6.0 (Table 6-14). Some blue-green, diatom and chrysophyte genera did occur more frequently from 1974 to 1976, but in terms of community richness this was offset by less frequent observations of cryptomonads. Richness did increase somewhat after lake pH declined in 1977 mainly because of increases in occurrences of chrysophyte and green genera. Reasons for this increase are unclear, but re-establishment of normal richness of phytoplankton communities of Sudbury-area acidic lakes follows additions of base by more than three years.

To compare the structures of the phytoplankton communities of the study lakes, correlation coefficients of the percentage contribution of the different algal classes to total biomass were calculated using data from untreated Clearwater Lake (see Table 1-9) and pre-manipulation data from the other study lakes (Table 6-14). The matrix of these correlation coefficients is presented in Table 6-15. Relative abundance of dinoflagellates was negatively correlated with relative abundance of chrysophytes and diatoms. Relative abundance of cryptomonads was negatively correlated with chrysophyte abundance. Chrysophyte and diatom relative abundances were positively correlated. As discussed in Chapter 1 these relationships are indicative of a replacement of diatom or chrysophyte dominated communities in the intermediately acidic lakes (Nelson and Joe) by cryptomonad and/or dinoflagellate dominated

Table 6-15: Matrix of correlation coefficients of percentage of ice-free period phytoplankton biomass contributed by algal classes including only premanipulation data. Data are from Clearwater Lake 1973-1978, Middle Lake 1973, Hannah Lake 1973-1974, Lohi Lake 1973, Nelson Lake Stations 1 and 4 - 1975, Swan Lake 1977 and Joe Lake 1976. Significance at 0.05 indicated by "*", at 0.01 by "**".

Percent	Cryptophyceae	Chlorophyceae	Chrysophyceae	Cyanophyceae	Bacillariophyceae
Dinophyceae	0.30	-0.31	-0.54*	-0.49	-0.77**
Cryptophyceae		-0.53	-0.57*	-0.28	-0.44
Chlorophyceae			0.02	0.16	0.08
Chrysophyceae				0.05	0.64*
Cyanophyceae					0.31

communities in the acidic lakes.

Correlation coefficients including pre- and post-neutralization data (excluding re-acidification data from 1977-1979 in Lohi Lake and post-fertilization data from Middle and Hannah Lakes) are presented in Table 6-16. Overall patterns were similar to those including only pre-manipulation data. The proportional abundance of dinoflagellates and cryptomonads were positively correlated. Relative abundance of dinoflagellates was negatively correlated with diatom and chrysophyte relative abundance as before, and cryptomonad relative abundance was again negatively correlated with the relative abundance of chrysophytes. Neutralization was accompanied by an increase in the relative abundance of chrysophytes in Lohi, Middle and Hannah Lakes and in diatoms in Nelson Lake but not in both algal classes in any one lake (Table 6-14). Therefore, chrysophyte and diatom relative abundances were not correlated when post-manipulation data were included (Table 6-16).

The return to communities dominated by chrysophytes or diatoms at the expense of cryptomonads or dinoflagellates (Fig. 6-11) after additions of base is a return to a pattern that is characteristic of non-acidic oligotrophic lakes in Ontario (see Chapter 1). Hillbricht-Ilkowska (1977) observed a similar trend in Lake Flosak in Poland. After the additions of base the contribution of chrysophytes increased from 1 to 28% while the contribution of dinoflagellates and cryptomonads declined from 35 to 16% of the phytoplankton biomass. It must be recalled, however, that three years after base additions, the richness of the phytoplankton community of Lohi Lake was still 2 to 3 times lower than that observed in non-acidified lakes.

Table 6-16: Matrix of correlation coefficients of percentage of ice-free period phytoplankton biomass contributed by algal classes including all pre and post neutralization data, with the exception of post-fertilization data from Middle and Hannah Lakes and data from Lohi Lake after its reacidification. Data are from Clearwater Lake 1973-1978, Middle Lake 1973-1974, Hannah Lake 1973-1975, Lohi Lake 1973-1976, Nelson Lake, Station 1 1975-1978, Station 4 1975-1977, Swan Lake 1977 and Joe Lake 1976. Significance of 0.05 indicated by "*", at 0.01 by "**".

Percent	Cryptophyceae	Chlorophyceae	Chrysophyceae	Cyanophyceae	Bacillariophyceae
Dinophyceae	0.44*	0.12	-0.44*	-0.31	-0.64**
Cryptophyceae		-0.16	-0.47*	-0.20	-0.36
Chlorophyceae			0.33	0.19	0.30
Chrysophyceae				0.02	0.11
Cyanophyceae					0.08

The relative abundance of dinoflagellates in Lohi Lake increased in 1977, the year that residual alkalinity in the lake was exhausted. This increase did not continue into 1978 and 1979 (Table 6-14) suggesting that there is a time lag of at least two years after lake pH drops below 5.0 before community assemblages that are typically associated with acidic lakes appear. In comparison with data from 1973, community structure in 1978 and 1979 was characterized by a higher relative abundance of chrysophytes, 28 and 40% in 1978 and 1979, respectively, vs. 2% in 1973. Chrysophytes, especially Mallomonas sp. and an unidentified chrysomonad were the most important contributors to total biomass in May and September of 1978 and in May, June, August and September of 1979 (Fig. 6-10). Greens were equally important after the reacidification of the lake as they were prior to additions of base in 1973. The dominant species was Oocystis submarina in 1973. In the spring and early summer of 1978, Staurastrum sp., Xanthidium sp. and Kirchneriella contorta were most important while K. contorta and Gloeocystis vesiculosa were the dominant greens in the fall of 1979.

Blooms of planktonic diatoms are certainly not considered to be characteristic of acidic lakes, although many diatom species are very tolerant of acidic environments. However, the highest phytoplankton biomass recorded in Lohi Lake occurred on June 12, 1979 when a Rhizosolenia longiseta population with an abundance of 12,700 cells mL^{-1} and a biomass of 7.3 mg L^{-1} occurred (Fig. 6-10). Rhizosolenia had not been recorded on the sampling dates immediately preceding (June 7) or following (June 19) June 12, nor in fact, was the genus recorded on any other sampling date from 1973-1979. Volumetrically-derived biomass undoubtedly overestimates the real biomass of Rhizosolenia because of its extremely large vacuole. For this reason data from June 12 were not included in the summarized phytoplankton statistics (Table 6-14).

viii. Zooplankton

Prior to additions of base the average number of species of crustacean zooplankton observed per collection (species richness) in Middle, Hannah and Lohi Lakes was about one-half of the number observed in Nelson Lake and about one-third of the number observed by Yan and Strus (1980) in non-acidic, oligotrophic lakes in the Haliburton-Muskoka area (Table 6-17). As in Clearwater Lake (Chapter 1) the most frequently observed species were *Cyclops vernalis*, *Chydorus sphaericus* and *Bosmina longirostris*. *B. longirostris* comprised the largest fraction of the biomass in Middle and Lohi Lakes as it did in Clearwater Lake. It was also dominant in Hannah Lake prior to base additions, although pre-manipulation community biomasses in Hannah Lake were an order of magnitude lower than in Middle or Lohi Lakes, most probably because of metal toxicity (Yan and Strus 1980). Copepods are apparently more tolerant of metals than are cladocerans (Baudouin and Scoppa 1974), although Borgmann *et al*. (1980) indicated that the difference in tolerance may be overestimated by studies of acute toxicity. This is perhaps why copepods were more important contributors to total biomass in Hannah Lake than in Middle or Lohi Lakes (Table 6-17).

Yan *et al*. (1977) demonstrated that prior to the additions of base, the zooplankton community of Nelson Lake was not different from that of non-acidic, oligotrophic lakes despite the pre-manipulation pH of 5.7. Additions of base had no immediate or long-term affects on the zooplankton of Nelson Lake.

In Middle, Hannah and Lohi Lakes, additions of base resulted in a slight decrease in species richness (Table 6-17) and in

Table 6-17: A summary of selected data on planktonic crustacea from Lohi, Middle, Hannah and Nelson Lakes. Data from Clearwater Lake are presented for comparison.

Lake	Year	pH	No. of Species per collection	Density (animals L^{-1})	Biomass (mg m^{-3})	Percent Biomass					
						Nauplii	Cyclopoda	*D. minutus*	Other Calanoida	*B. longirostris*	Other Cladocera
Clearwater	1973-1978	4.27	3.7	11.9	8.58	6.1	5.7	<0.1	<0.1	87.1	1.1
Lohi	1973[1]	4.39	3.6	36.0	24.0	13.1	5.6	0	0	80.7	0.6
	1974	6.04	3.1	1.38	1.17	<0.1	16.2	5.1	0.3	76.1	2.3
	1975	6.09	3.0	1.18	0.65	34.7	18.1	0	0	40.4	6.8
	1976	6.09	3.3	10.8	7.96	7.2	15.6	<0.1	0	76.6	0.6
	1977	5.27	3.0	5.90	4.14	9.4	15.3	0.5	0	74.7	0.1
	1978	4.79	4.1	26.5	27.0	10.0	0.5	84.9	<0.1	4.4	0.2
	1979	4.74	2.5	33.7	35.1	10.0	<0.1	87.3	0	2.6	<0.1
Middle	1973[1]	4.40	3.4	19.7	13.7	6.3	1.2	0	0	92.0	0.5
	1974	7.01	2.7	0.56	0.88	0.2	67.3	0	9.0[3]	20.5	3.0
Hannah	1973	4.31	2.9	1.11	0.68	24.8	4.3	0	0	59.6	11.3
	1974	4.29	3.1	0.64	0.71	0.3	33.5	0	20.5[3]	34.8	7.5
	1975[2]	7.02	2.4	0.15	0.07	50.4	25.9	0	0	3.3	20.4
Nelson 1	1975[1]	5.73	6.9	36.4	34.0	24.5	31.2	39.6[4]	0	2.8	1.9
	1976	6.35	5.5	32.1	41.5	9.2	39.9	34.1[4]	0	11.5	5.3
4	1975	5.73	6.2	44.5	55.1	8.1	32.8	49.5[4]	0	1.4	8.2
	1976[2]	6.14	6.3	41.4	71.5	6.3	62.5	23.2[4]	0	4.4	3.6

[1] pre-manipulation data only
[2] post-manipulation data only
[3] unidentified copepodid
[4] assuming all copepodids are *D. minutus*, the only identified calanoid in the lake.

immediate and drastic reductions in standing stocks. In Lohi Lake community biomasses did not show signs of recovering for two full years after additions of base. In Middle and Hannah Lakes, additions of phosphorus followed additions of base by less than two years and responses to these additions are discussed later.

In Lohi Lake, the density and biomass of the zooplankton community were 36 animals L^{-1} and 24 mg m^{-3}, respectively, prior to additions of base in 1973. Standing stocks did not appreciably recover from base additions until 1976 even though phytoplankton biomass had, by 1974 recovered to levels similar to those of 1973. Species richness had not increased by 1977, the year when the added alkalinity was exhausted and average pH fell to 5.3. This suggests that once eliminated from lakes by depressed pH and high heavy metal levels, more than four years are required for the re-establishment of species of planktonic crustacea typically observed in non-acidic Shield lakes. Bengtsson et al. (1980) indicated that re-colonization of limed lakes in Sweden by species of zooplankton typically associated with non-acidic lakes also took a number of years. In contrast, Hillbricht-Ilkowska et al. (1977) observed that the diversity of the crustacean zooplankton community of humic lake Flosak in Poland increased within one year of additions of base.

In 1978 and 1979, the pH of Lohi Lake fell below 5.0 and the structure of the community changed completely. The contribution of B. longirostris to total biomass fell to <5%. It had contributed 40 to 81% of the biomass in all previous years. The reason for this decrease was the appearance of Diaptomus minutus in the community. Although present in low numbers in 1974, D. minutus was not observed in the lake from 1975 to 1977. In 1978 and 1979 D. minutus was the dominant crustacean in the lake (Fig. 6-12), forming over 80% of the biomass (Table 6-17). Densities of D. minutus were comparable with those reported in non-acidic, oligotrophic lakes in Canada (Schindler and Noven 1971, Davis 1972). Crustacean densities and biomasses in 1978 and 1979 in Lohi Lake were similar to those of 1973 (Table 6-17), and approach those recorded in non-acidic Shield Lakes, although zooplankton densities were depressed in the other study lakes that were acidic and contaminated with trace metals (Yan and Strus 1980).

It is difficult to determine why D. minutus replaced B. longirostris as the dominant zooplankter in Lohi Lake after the lake reacidified. Both species are commonly observed in acidic lakes in Ontario although D. minutus is more commonly dominant. Sprules (1975) observed B. longirostris in 17 of 28 La Cloche Mountain Lakes of pH <5.0. It was dominant in 9 of these lakes and was the second most abundant species. The most abundant was D. minutus which was dominant in 27 of the 28 lakes. Keller (1981) observed that D. minutus and B. longirostris were the only two taxa to occur in all 21 sampled lakes with pH <5.0 in the greater Sudbury area. They were dominant in 90 and 62% of the lakes, respectively.

The change from a community dominated by B. longirostris prior to base additions to one dominated by D. minutus after reacidification is probably not a consequence of differences in lake chemistry. Levels of pH (Table 6-2), TP (Table 6-9) and TN (Table 6-10) observed in 1978 and 1979 were similar to levels in 1973. Differences between the two periods in lake transparency (Table 6-11) and temperature (Appendix 5) were small. Levels of Cu were slightly lower in 1978 (71 μgL^{-1}) than in 1973 (84 μgL^{-1}) while levels of Ni and Zn were very similar. Concentrations of Al were most probably reduced about 3-fold. Levels were 160 μgL^{-1} in

1978, and while not measured in 1973 in Lohi Lake, levels would have been similar to the 480 $\mu g L^{-1}$ measured in Clearwater Lake. Al is an order of magnitude less toxic than Cu to zooplankton, (Biesinger and Christensen 1972), however, and there is no evidence to suggest that *D. minutus* should be more sensitive to Al than *B. longirostris*. The reverse, in fact, is more probably true, (Baudouin and Scoppa 1974) suggesting that changes in metals could not be responsible for changes in zooplankton community structure.

B. longirostris and *D. minutus* are herbivores with the latter species apparently preferring slightly larger food particles (Gliwicz 1969). The increase in proportional abundance of *D. minutus* which occurred in the spring of 1978 (Fig. 6-12) occurred without any obvious changes in size ranges of available prey (phytoplankton). Species that, based on size, would have been available to both herbivores occurred in abundance. Dominant algae at that time were a small (6 µm x 9 µm) unidentified dinoflagellate, *Chlamydomonas* sp. and a small unidentified chrysomonad.

Confer and Cooley (1977) demonstrated that rates of naupliar mortality observed for *D. minutus* in Bluff Lake, Nova Scotia, could be explained by the predation by omnivorous copepods, *Mesocyclops edax* and *Epischura nordenskioldi*. Increases in densities of *D. minutus* might then be attributable to reductions in rates of predation, if densities of invertebrate predators were reduced in 1978 and 1979.

C. vernalis is the major planktonic predator in Lohi Lake. Densities of this organism were reduced by base additions in 1974 and 1975, then recovered to pre-manipulation levels in 1976 and 1977 (Fig. 6-13). Densities were in fact reduced in 1978 and the animals were virtually absent (and thus their densities were not plotted) in 1979.

There is unfortunately no agreement in the literature on prey choice by cyclopoid copepods; hence, a prediction of the affects of reductions in abundances of *C. vernalis* on herbivorous community structure is very difficult. Efficient predation by *C. vernalis* on *B. longirostris* has been observed in the field (Kerfoot 1977) and in the laboratory (Brandl and Fernando 1974) suggesting that a decline in abundance of *C. vernalis* could have favoured *B. longirostris*. Anderson (1970), however, demonstrated that *C. vernalis* and *C. bicuspidatus thomasi* preyed readily on nauplii and young copepodids of the calanoids *Diaptomus sicilis* and *Diaptomus tyrelli*. *C. vernalis* consumed more prey than *C. bicuspidatus thomasi*. When exposed to their own nauplii, to *D. sicilis* copepodids and to the small cladoceran *Ceriodaphnia quadrigula*, IV and V stage copepodids of *C. bicuspidatus thomasi* preyed preferentially upon the cladoceran, not upon the copepodids. In contrast, Brandl and Fernando (1978) indicated that while *Cyclops vicinus* and *Mesocyclops edax* would prey on both *B. longirostris* and nauplii of calanoid copepods, the proportion of nauplii captured was significantly higher than the proportion of nauplii offered. The reverse was true for *B. longirostris*. Evidence for efficient predation on calanoid nauplii and on *B. longirostris* by cyclopoid predators, therefore exists, and effects of reduced predation on a competitive interaction of *B. longirostris* and *D. minutus* is impossible to predict.

While there is no simple explanation for the replacement of *B. longirostris* by *D. minutus* it is possible that a subtle interaction of factors may have been responsible for the change. Alternatively, the dominance in acidic lakes by *D. minutus* or *B. longirostris* may represent alternately stable communities. This has been suggested by Sprules (1972) to explain the allopatric occurrence of two Daphnia species in two ponds that were geographically close and otherwise similar in zooplankton community structure.

ix. Fish

Acidification of sensitive lakes in Scandinavia and in the United States has resulted in losses of fish populations (reviewed by Scofield 1976). In Ontario, Beamish and Harvey (1972), Beamish *et al*. (1975) and Harvey (1975) have demonstrated that the extinction of many fish species from a large number of lakes located in the LaCloche Mountains, south-west of Sudbury was attributable to acidification. Of 209 lakes surveyed as part of the Sudbury Environmental Study extensive monitoring program, 20% had pH <5.5. Lake and brook trout populations in a large fraction of these lakes were absent or imperilled (Ont. Min. Environ. 1978).

In 1972 staff of the Ministry of Natural Resources evaluated the status of the fisheries in Middle, Lohi, Hannah and Clearwater Lakes. No fish were caught in these lakes after 66, 91, 94 and 213 hours, respectively, of fishing efforts with 2800 feet of net laid in each lake. The demise of the fisheries was attributable to low pH and/or high levels of metallic toxicants. As additions of base raised the pH and decreased metal levels in the study lakes, the potential for re-establishing fish communities in these lakes was investigated, initially in on-shore bioassays. Baksi *et al*. (1978) reported results of experiments conducted in 1975 evaluating survival times of pumpkinseed sunfish, fathead minnows and rainbow trout in Hannah Lake and Lohi Lake in comparison with Lake Panache, a lake known to support a viable fishery. In 15-day exposures, survival times of the first two test species were not different among the three lakes. The experiments with rainbow trout were inconclusive as temperatures in the test tanks reached levels lethal to salmonids.

Powell (unpublished studies) stocked Middle Lake with 2500 "young-of-the-year" smallmouth bass (*Micropterus dolomieui*) in August, 1976 following earlier stocking (June 1976) with 500 Iowa darters (*Etheostoma exile*) and 200 brook stickleback (*Culaea inconstans*). At the time, lake pH was 6.2 and total Cu, Ni and Zn concentrations were 60, 470 and 35 $\mu g\ L^{-1}$, respectively. Despite considerable fishing effort (eight plastic traps for 193 hours, 12 trap nets for 290 hours and 2 gill nets for 51 hours) in June of 1977, Powell failed to capture a single bass.

Similarly, Powell (1977) stocked Lohi Lake in April, 1976 with 1200 yearling brook trout (*Salvelinus fontinalis*), 1400 Iowa darters and 170 brook stickleback. Lake pH at that time was 6.2 and total Cu, Ni and Zn concentrations were 40, 160 and 32 $\mu g\ L^{-1}$, respectively. After failing to recapture any trout in 140 hours of gill netting effort four months after the fish had been introduced, he concluded that all of the brook trout had died. Mortality was primarily attributed to copper toxicity.

In order to test the assumption that complete mortality had occurred and that elevated concentrations of Cu in the lake had resulted in the deaths, experiments providing recovery of all test organisms were necessary. Experiments of this nature were performed in Middle and Lohi Lakes in 1977 and have been described previously (Yan *et al*. 1979). Results are summarized below.

In 1977, yearling rainbow trout were planted in $2m^3$ enclosures suspended within the metalimnia of Panache, Middle and

Lohi Lakes. Rates of mortality of trout were very rapid in Middle and Lohi Lakes. Geometric mean survival times (GMST) were 3.6 and 2.3 days in Middle and Lohi Lake enclosures, respectively (Table 6-18), and were not increased by acclimation to the low heavy metal concentrations of the holding pool in Lake Panache. GMST was an order of magnitude higher in Lake Panache (Table 6-18). Lake pH values were not low enough to have resulted in the observed mortalities. As GMST was correlated with metal concentrations of the lake and as rates of accumulation of metals into liver and gill tissues of exposed fish were much higher in Lohi and Middle Lakes than in Lake Panache, it is probable that the fish died because of metal toxicity. Despite reductions in heavy metal concentrations that accompanied experimental neutralization of the lakes, levels of Cu and possibly also of Zn, Al and Ni acting in conjunction with the copper, were high enough to have resulted in the observed mortalities.

These experiments supported the conclusion of Powell (1977) that all the brook trout stocked into Lohi Lake in 1976 had died. They further indicated that despite the reductions in metal concentrations that accompanied additions of base, the water quality of Middle and Lohi Lakes in 1977 was not suitable for the re-establishment of fisheries. In 1979 the pH of Lohi Lake was lower than in 1977 (Fig. 6-1) and metal levels had increased (Fig. 6-5). Water quality had clearly not improved. While metal concentrations in Middle Lake had declined in 1980, they were still above levels considered to be required for the long-term survival of trout (McKim and Benoit 1971).

Bengtsson et al. (1980) reported that in Sweden, lime was added to 700 lakes and rivers between 1977 and 1979. Evidence was

Table 6-18: Number of experiments (No.), selected chemistry of lakes during experiments and geometric mean survival time (GMST) of rainbow trout (from Yan *et al*. 1979) in selected S.E.S. lakes.

Lake	No.	pH	Al	Cu	Ni	Zn	GMST (days)
			(mg m^{-3})				
Middle	5	6.4	53	53	406	27	3.6(2.1-5.7)[2]
Lohi	3	5.3	97	43	227	31	2.3(1.3-3.5)[2]
Panache	1[1]	6.5	-	6	28	6	34.0

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[1] In this experiment fish were placed in transportation enclosure and driven over local roads for 2 hours prior to being placed into enclosures. In a later experiment fish were taken from the holding pool on the shores of Lake Panache and placed directly into the enclosure. No mortalities were observed for 50 days in this experiment, indicating that fish survival in the enclosures was possible given suitable water quality.

[2] range for experiments in parenthesis.

presented that fisheries had responded positively to these additions. Young salmon were caught in the Hiegsvadsan River, for example, only after depressions of pH at times of high flow had been stopped by additions of base. These efforts suggest that additions of base may be more effective in waters that are not also contaminated with metals such as Cu.

While levels of Cu were much lower prior to additions of base in Nelson Lake than in Middle, Hannah or Lohi Lakes, Powell (1976) indicated that fisheries were in a state of decline in Nelson Lake prior to base additions. The fish community was dominated by yellow perch. Smallmouth bass, a species previously reported in the lake, had disappeared in the mid 1960's. Beamish (1974) reported that smallmouth bass was replaced by yellow perch in moderately acidic George Lake in the La Cloche Mountains.

The effects, if any, of base additions on the fish community of Nelson Lake are difficult to assess. Lake trout and white suckers produced good year classes in 1975 before base additions, and in 1976 after additions. Extremely heavy fishing pressure in the winter of 1979-1980 makes long term evaluations of the effects of base additions on trout populations very difficult. While changes in trout populations are difficult to evaluate, there appears to have been a substantial change from 1975 to 1980 in the inshore fishery. Thirty adult smallmouth bass were introduced into the lake in 1978 by Ontario Ministry of Natural Resources personnel. Successful spawning and fry emergence were observed at the only nest located. Numbers of perch and brown bullhead captured in trap nets at six sites have declined since 1975 while catches of smallmouth bass have increased in 1980 for the first time (J. Gunn, unpub. data). These changes indicate a qualitative improvement in the fisheries status of Nelson Lake.

D. Summary

1. The pH of Middle, Lohi and Hannah Lakes was raised by additions of base from 4.3 - 4.4 to near neutrality. In Middle and Hannah Lakes, average pH remained >6.5 until the end of the study (1980), while in Lohi Lake, added acid neutralizing capacity (ANC) was exhausted in the spring of 1977. At that time the pH of the lake was 5.4. By 1979 the pH had decreased to 4.7. The pH of Lohi Lake decreased because: a) it received a higher volumetric supply of acid than did Middle and Hannah Lakes, b) concentrations of ANC remaining immediately after additions of base were much lower in Lohi Lake than in Middle and Hannah Lakes, and c) fertilization of Middle and Hannah Lakes resulted in generation of more alkalinity than was generated by the biota in Lohi Lake.
2. In Middle, Lohi and Hannah Lakes, 30-41% of the added ANC was consumed by reaction with Al^{3+}, Cu^{2+} and Ni^{2+}, 1-3% by hydroxylation of trace metals other than Al, Cu and Ni, 5-20% by direct reaction with H^{+}, and, by residual, 31-44% by neutralization of acidic sediments.
3. Additions of base significantly reduced levels of Cu, Ni, Mn, Al and Zn in Middle, Lohi and Hannah Lakes. Metal concentrations in the lakes were controlled by pH-dependent solubility reactions, not by external input rates; hence, levels of Cu, Ni, Zn and Mn in Lohi Lake returned to pre-treatment levels after the lake re-acidified.
4. Additions of base produced no long-term changes in concentrations of TP or TN.

5. The addition of base was followed by an immediate and drastic reduction in phytoplankton standing stocks in Middle, Lohi and Hannah Lakes. Levels recovered to approach, but not exceed, pre-treatment levels within a few months. While taxa that are characteristically dominant in non-acidic lakes (chrysophytes) replaced acid-tolerant species (dinoflagellates) after community biomasses recovered, community richness remained well below normal for the duration of the study. Dinoflagellates did not replace chrysophytes after the re-acidification of Lohi Lake, indicating that there is at least a 2-year lag before communities typical of acidic lakes are re-established.

6. Secchi transparency increased immediately after additions of base, accompanying the large decrease in phytoplankton standing stocks. In the long-term, however, Secchi transparency decreased by 2m in Lohi Lake after neutralization, then increased to pre-neutralization levels after the lake re-acidified. These longer term changes were not correlated with changes in phytoplankton standing stocks. The decrease in transparency after neutralization resulted in a shallower mixing zone and a cooler hypolimnion. It also reduced the depth of maximum photosynthetic activity.

7. Additions of base drastically reduced zooplankton standing stocks in Middle, Hannah and Lohi Lakes. Biomass did not recover for 2 years in Lohi Lake and communities typical of non-acidic lakes had not been re-established 4 years after the additions of base, when the lake re-acidified.

8. Rainbow trout were placed in submerged enclosures in Middle and Lohi Lakes after additions of base. They survived for less than 4 days, on average. Despite the reduction in levels of trace metals that had occurred after additions of base, levels of metals, especially Cu, were too high to allow survival of the fish.
9. Additions of base raised the pH of Nelson Lake from 5.7 to 6.3. The addition significantly reduced levels of Cu, Ni, Mn, Al and Zn, but produced no short or long-term changes in nutrient chemistry or in assemblages of plankton.

LIST OF FIGURES

Note: The following symbols have been used in all figures in Chapter 6:

Symbol	Meaning
△	first date, or dates, of addition of $Ca(OH)_2$.
▲	first date, or dates, of addition of $Ca(OH)_2 + Ca(CO)_3$.
◆	first date or dates of addition of P (to Middle and Hannah Lakes), and P and/or N (to Mountaintop and Labelle Lakes).

Fig. 6-1. Seasonal changes in whole-lake (1 m below surface in 1974) pH of 4 study lakes.

Fig. 6-2. Mean, annual whole-lake concentrations of sodium and chloride in Middle and Hannah Lakes. Samples in 1974 were taken at 1 m below surface.

Fig. 6.3. Mean, annual whole-lake concentrations of sodium and chloride in Clearwater and Lohi Lakes. Samples in 1974 were taken at 1 m below surface.

Fig. 6-4. Seasonal changes in pH of Nelson Lake, station 1 (main basin) and station 4 (northwest basin).

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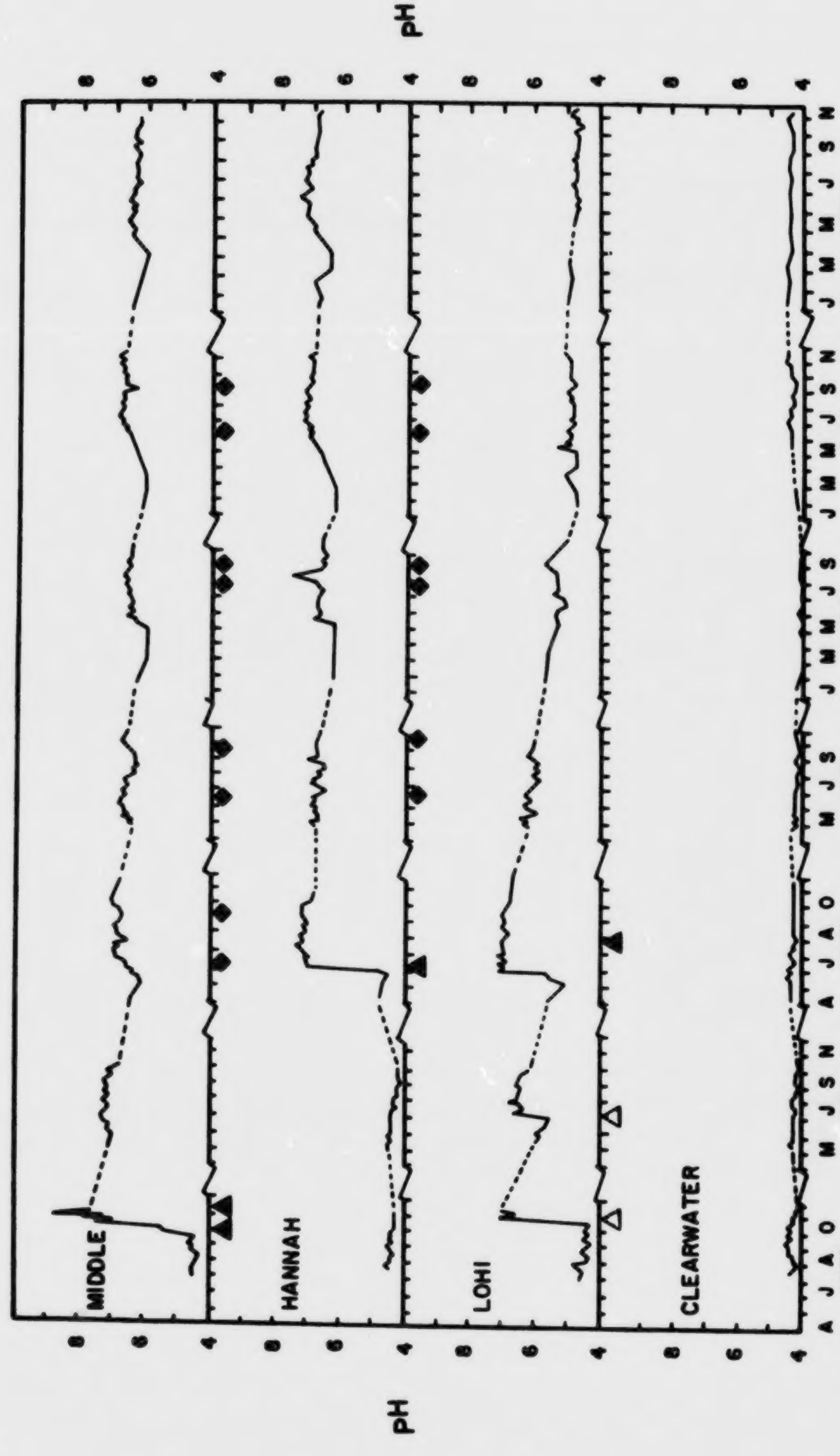
Fig. 6-11. Percentage of phytoplankton biomass (averaged over the ice-free period) comprised by Dinophyceae + Cryptophyceae or Chrysophyceae + Bacillariophyceae vs. pH. Data are 1973-1978 for Clearwater Lake (●), 1973-1976 for Lohi Lake (x), 1973-1974 for Middle Lake (△), 1973-1975 for Hannah Lake (▲), 1975-1978 for Nelson Lake stations 1 (O) and 4 (◇), 1977 for Swan Lake (◆) and 1976 for Joe Lake (□).

Fig. 6-12. Seasonal variations in densities of _Bosmina longirostris_, _Diaptomus minutus_ and calanoid copepodids in Lohi Lake from 1973 to 1979.

Fig. 6-13. Seasonal variations in densities of _Cyclops vernalis_ and cyclopoid copepodids in Lohi Lake from 1973 to 1978. Densities were <0.1 animals L^{-1} in 1979 and were not plotted.

Fig.6-1



pH
8
6
4
MIDDLE
HANNAH
LOHI
CLEARWATER
A J A O
1973
M J S N
1974
A J A O
1975
M J S
1976
J M M J S
1977
J M M J S N
1978
J M M J S N
1979

Fig.6-2

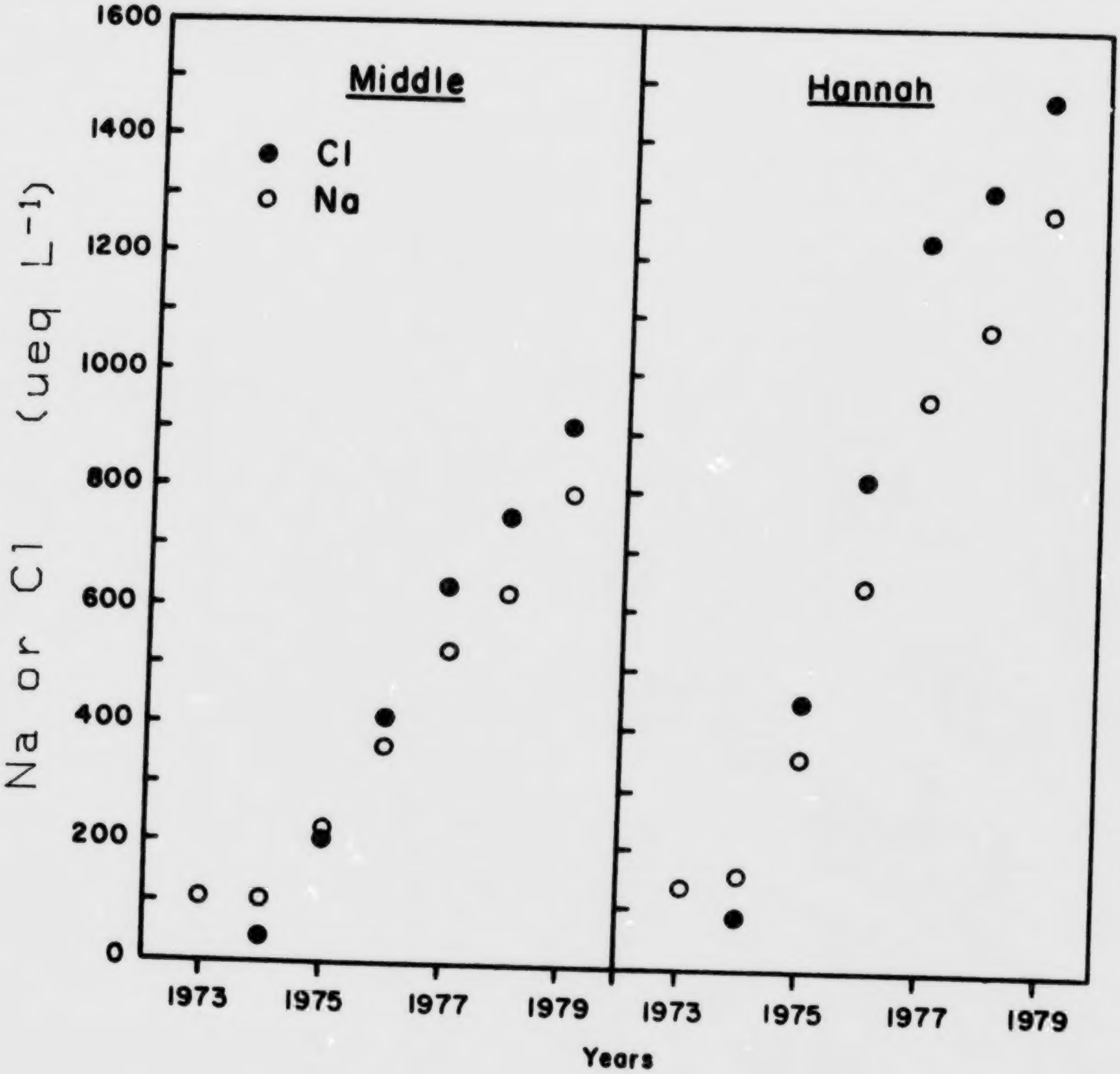

Middle
Hannah
● Cl
○ Na
Na or Cl (ueq L-1)
0
200
400
600
800
1000
1200
1400
1600
1973
1975
1977
1979
1973
1975
1977
1979
Years

Fig.6-3

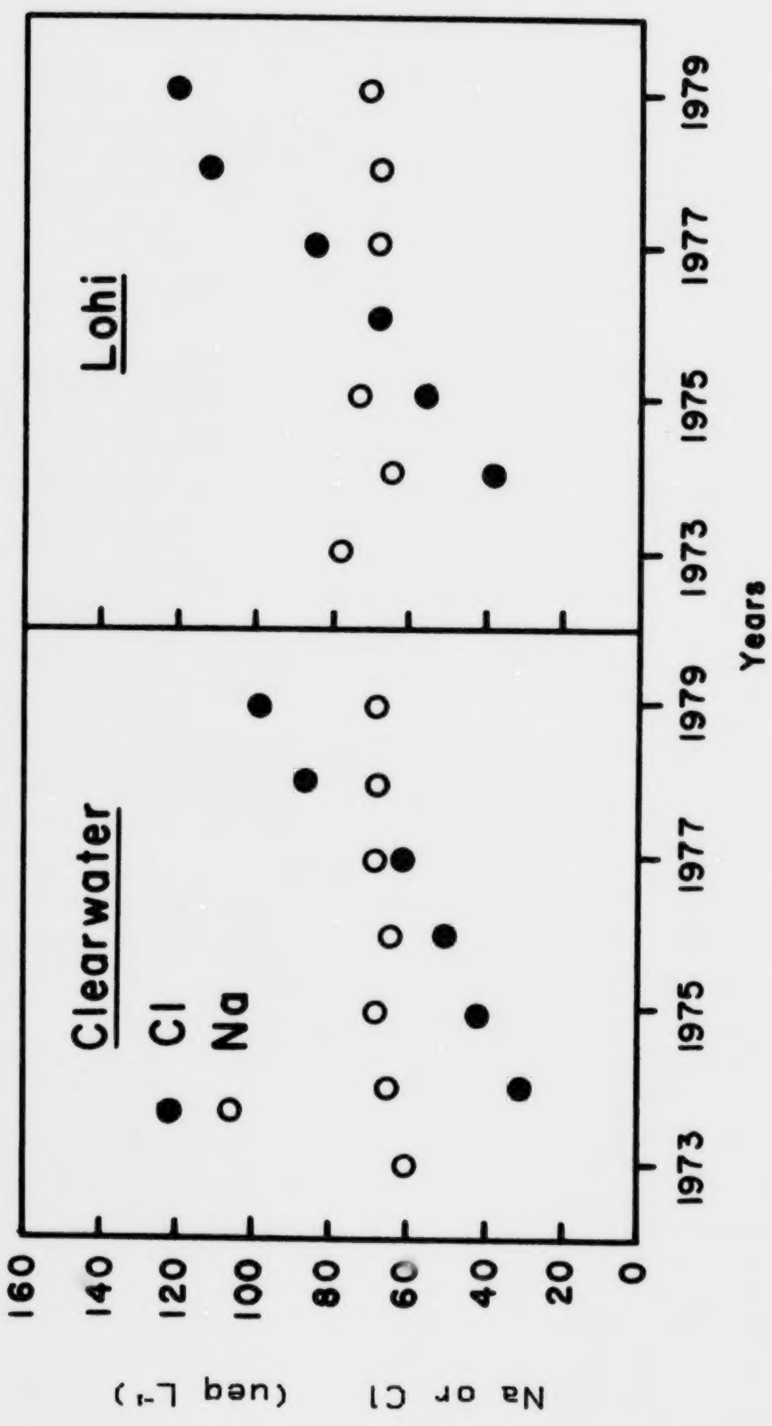

Clearwater
Lohi
● Cl
○ Na
160
140
120
100
80
60
40
20
0
1973
1975
1977
1979
1973
1975
1977
1979
Years
Na or Cl (ueq L-1)

Fig.6-4

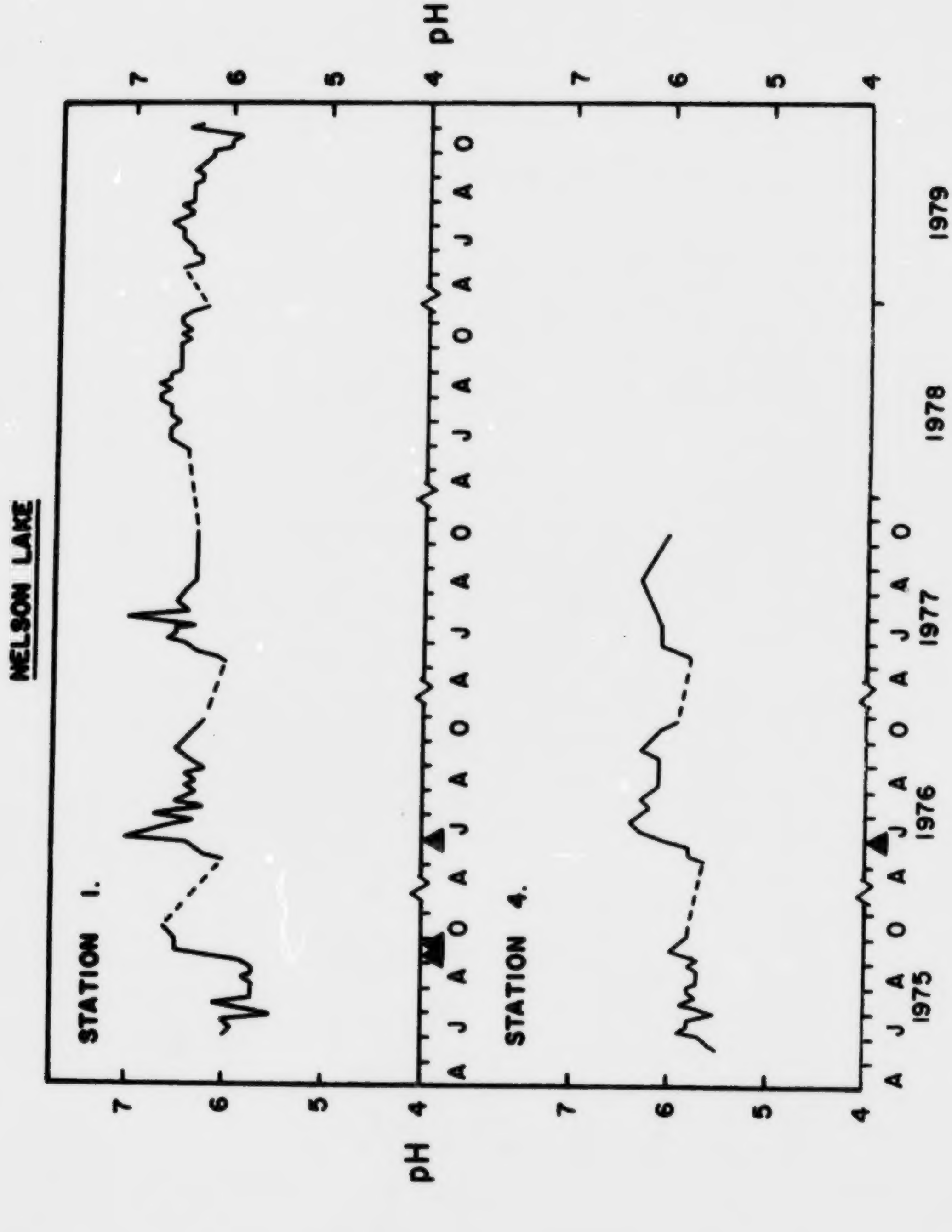

NELSON LAKE
STATION 1.
STATION 4.
pH
7
6
5
4
pH
A
J
A
O
1975
1976
1977
1978
1979

Fig.6-5

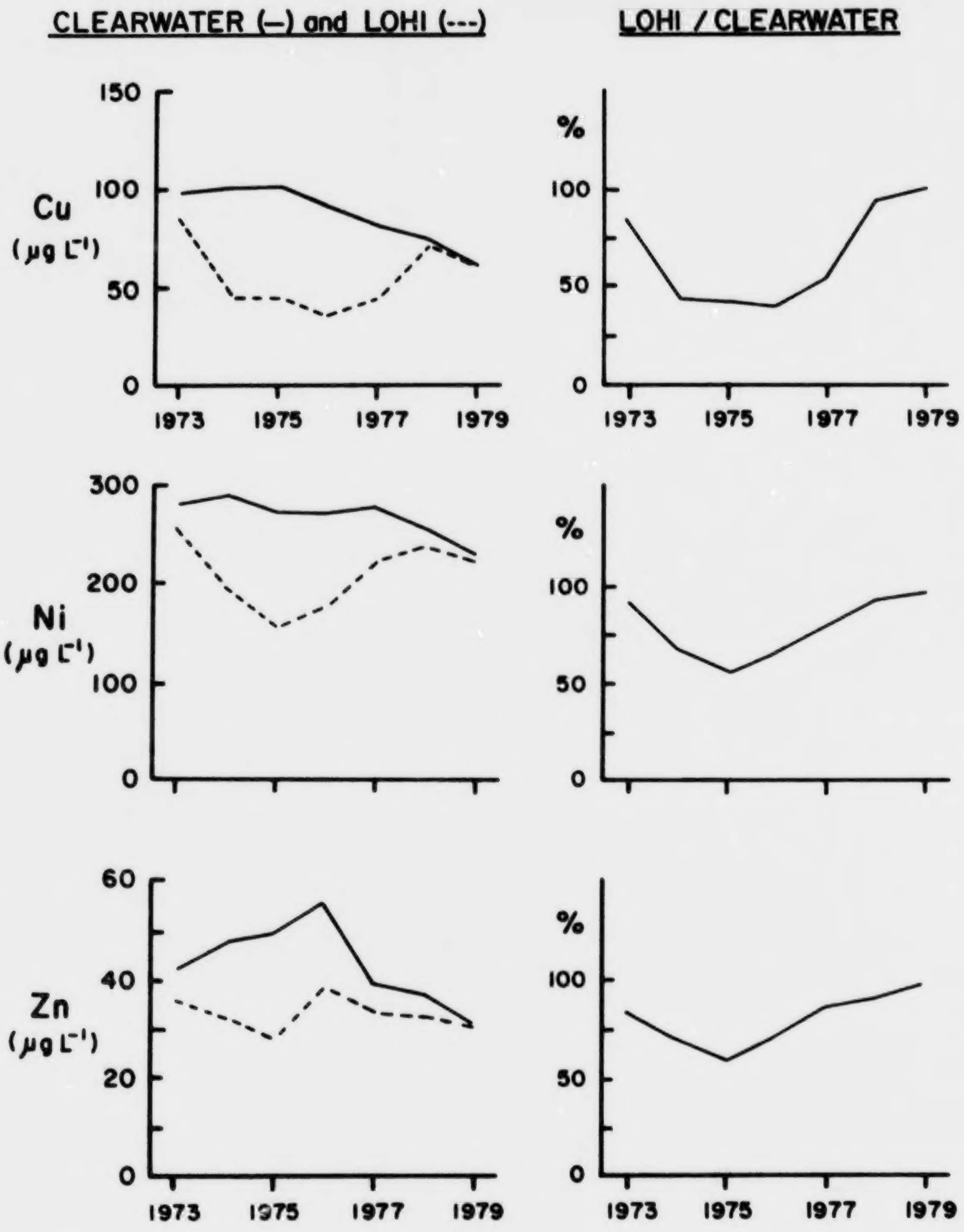

CLEARWATER (–) and LOHI (---)
LOHI / CLEARWATER
Cu
(µg L⁻¹)
Ni
(µg L⁻¹)
Zn
(µg L⁻¹)
%
150
100
50
0
300
200
100
60
40
20
1973
1975
1977
1979

Fig.6-5 (cont.)

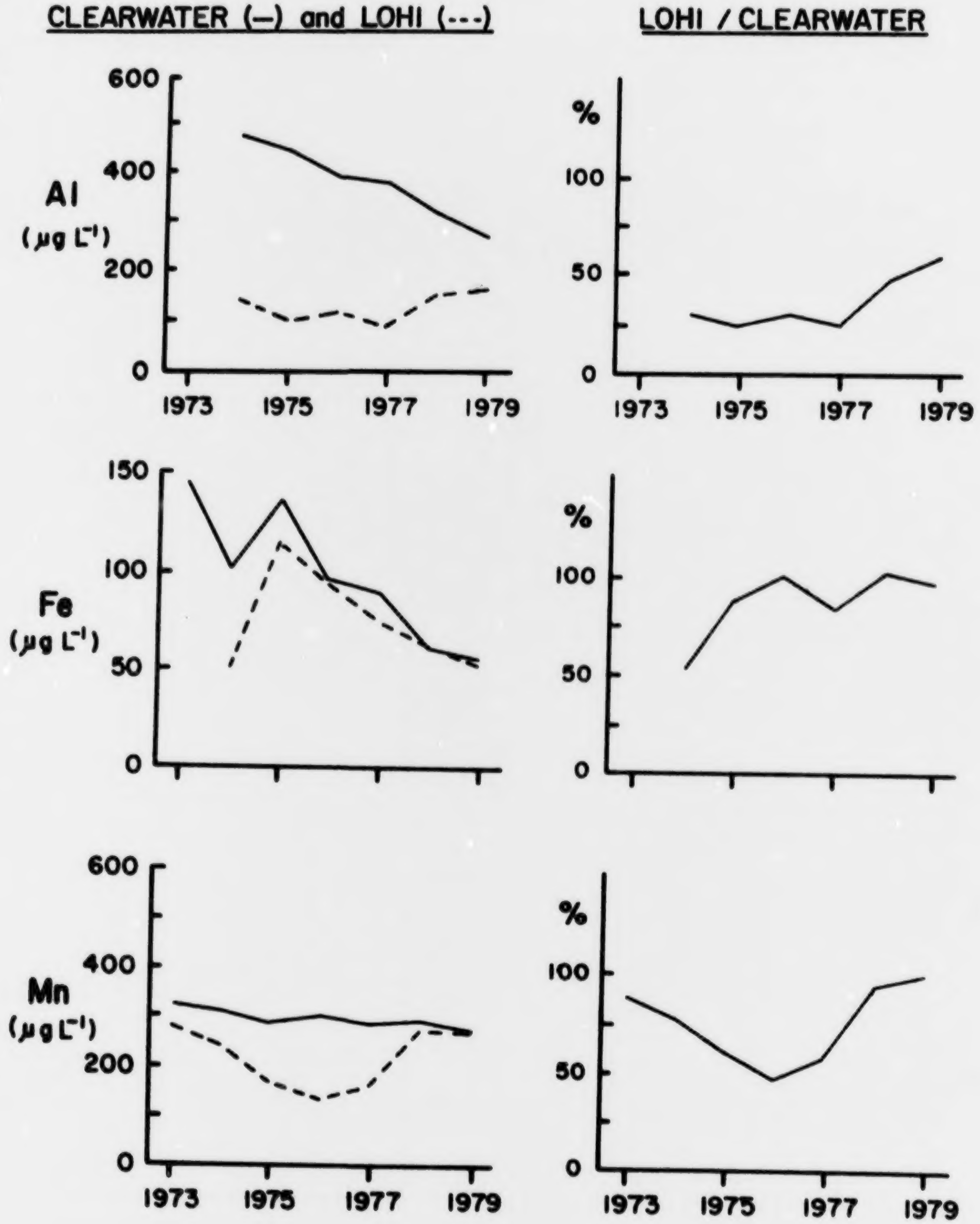

CLEARWATER (—) and LOHI (---)
LOHI / CLEARWATER
Al
(µg L⁻¹)
600
400
200
0
%
100
50
0
1973
1975
1977
1979
Fe
(µg L⁻¹)
150
100
50
0
%
100
50
0
Mn
(µg L⁻¹)
600
400
200
0
%
100
50
0
1973
1975
1977
1979

Fig.6-6

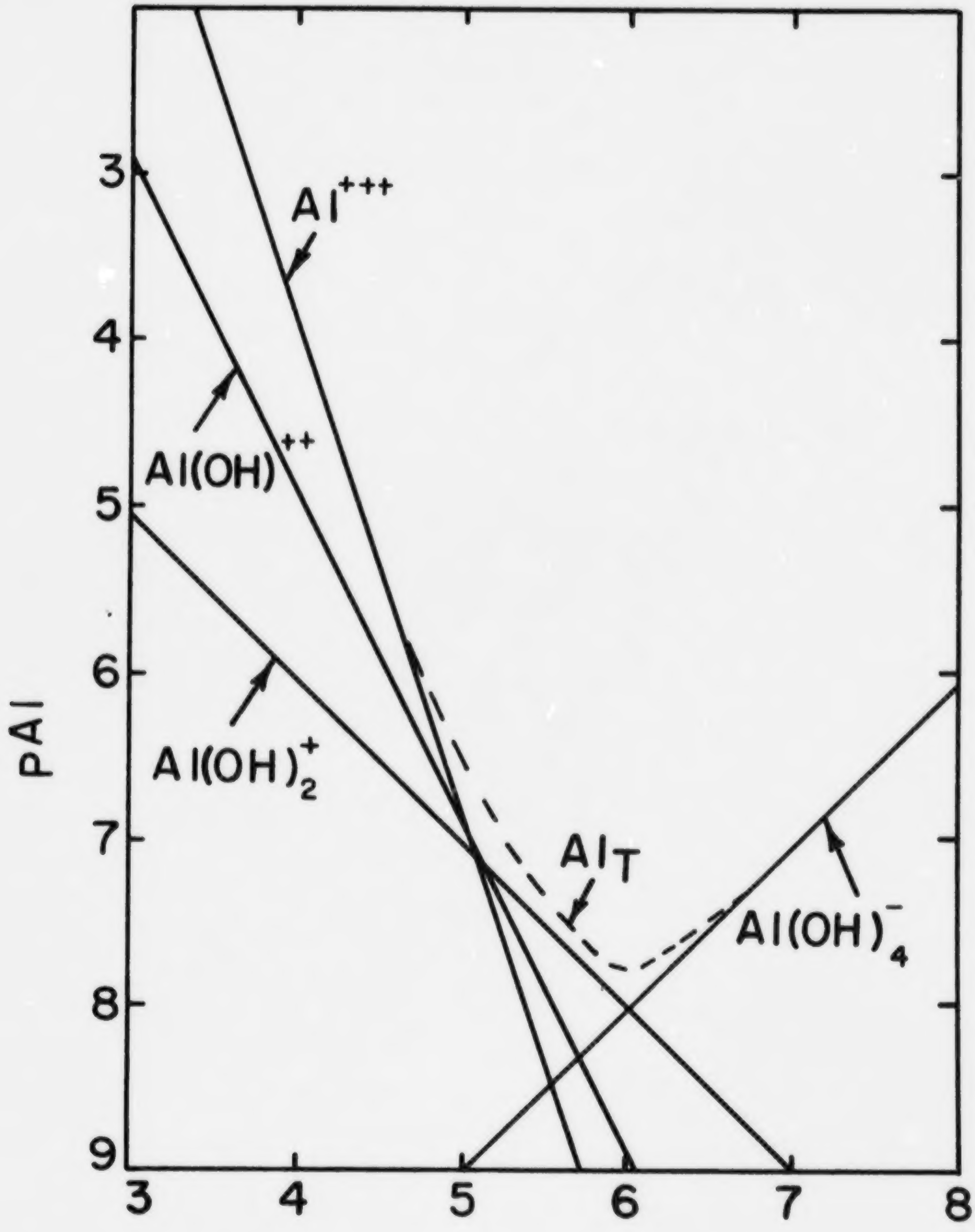


Fig.6-7

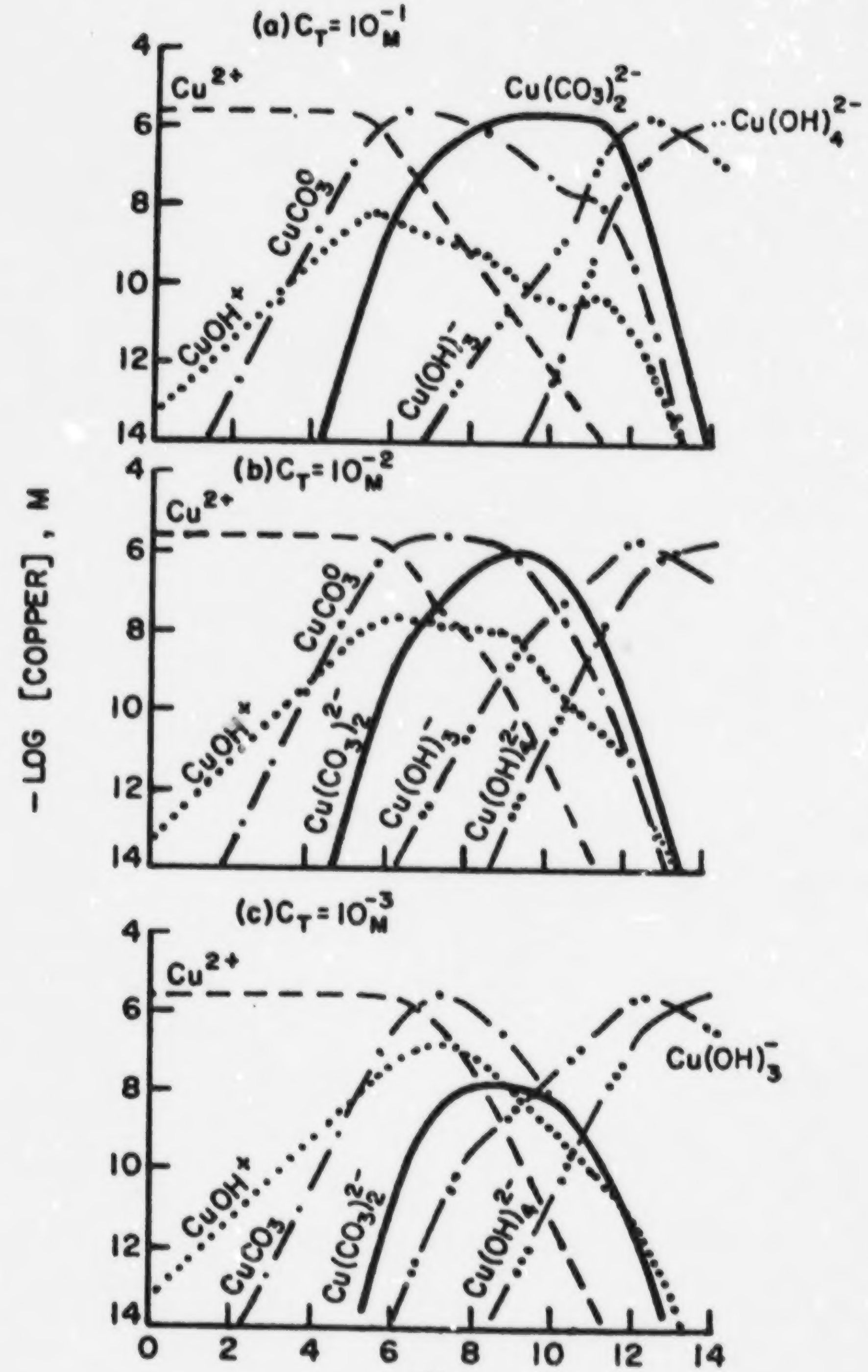

(a) $C_T = 10^{-1}_M$
Cu^{2+}
Cu(CO$_3$)$_2^{2-}$
Cu(OH)$_4^{2-}$
CuCO$_3^0$
CuOH$^+$
Cu(OH)$_3^-$
(b) $C_T = 10^{-2}_M$
Cu^{2+}
CuCO$_3^0$
CuOH$^+$
Cu(CO$_3$)$_2^{2-}$
Cu(OH)$_3^-$
Cu(OH)$_4^{2-}$
(c) $C_T = 10^{-3}_M$
Cu^{2+}
Cu(OH)$_3^-$
CuOH$^+$
CuCO$_3$
Cu(CO$_3$)$_2^{2-}$
Cu(OH)$_4^{2-}$
−LOG [COPPER], M
4
6
8
10
12
14
0
2
4
6
8
10
12
14
pH

Fig.6-8

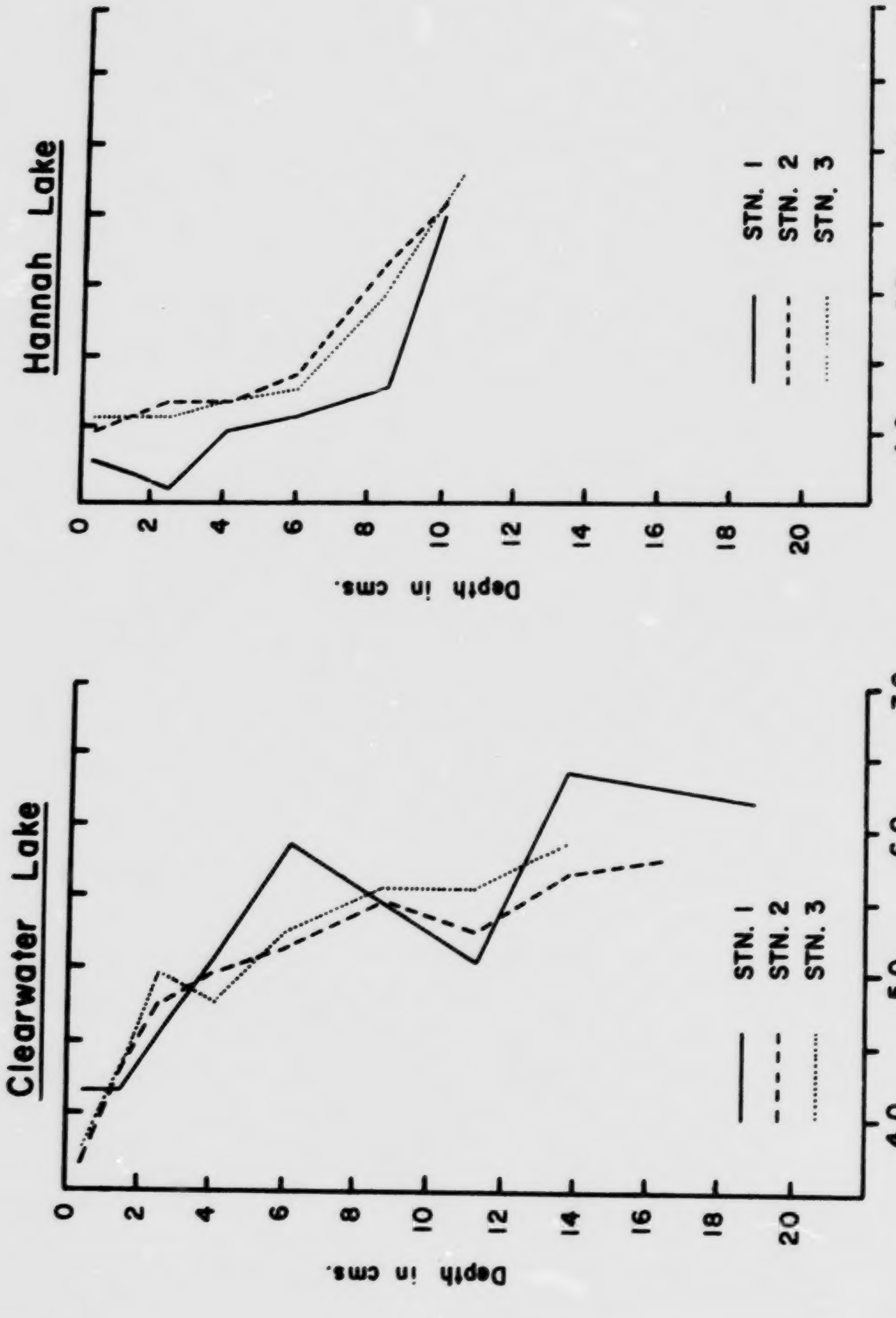
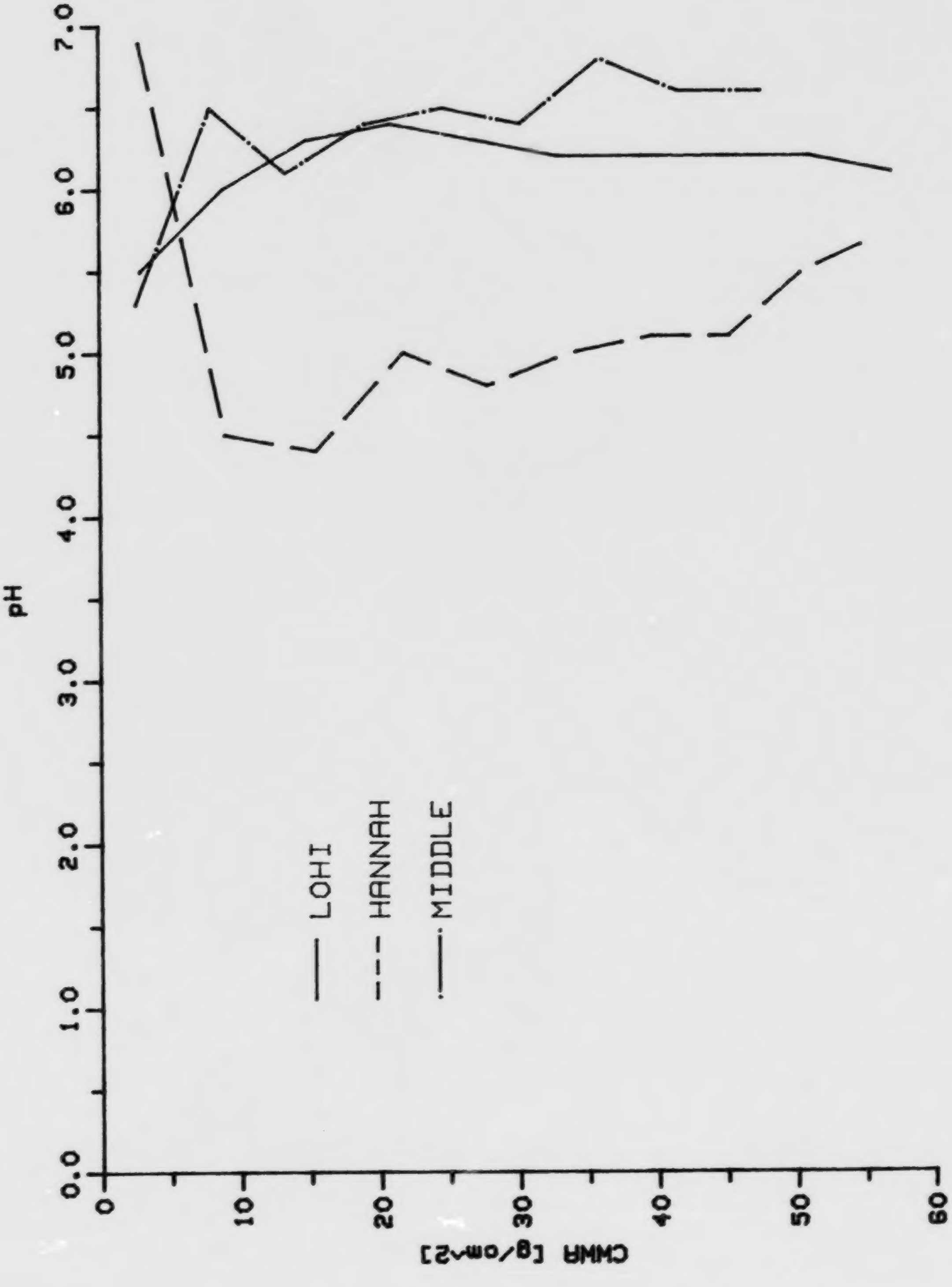

Clearwater Lake
Depth in cms.
0
2
4
6
8
10
12
14
16
18
20
pH
4.0
5.0
6.0
7.0
STN. 1
STN. 2
STN. 3
Hannah Lake
Depth in cms.
0
2
4
6
8
10
12
14
16
18
20
pH
4.0
5.0
6.0
7.0
STN. 1
STN. 2
STN. 3

Fig.6-9



pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0
10
20
30
40
50
60
CWWA [g/cm^2]
LOHI
HANNAH
MIDDLE

Fig.6-10

LOHI LAKE

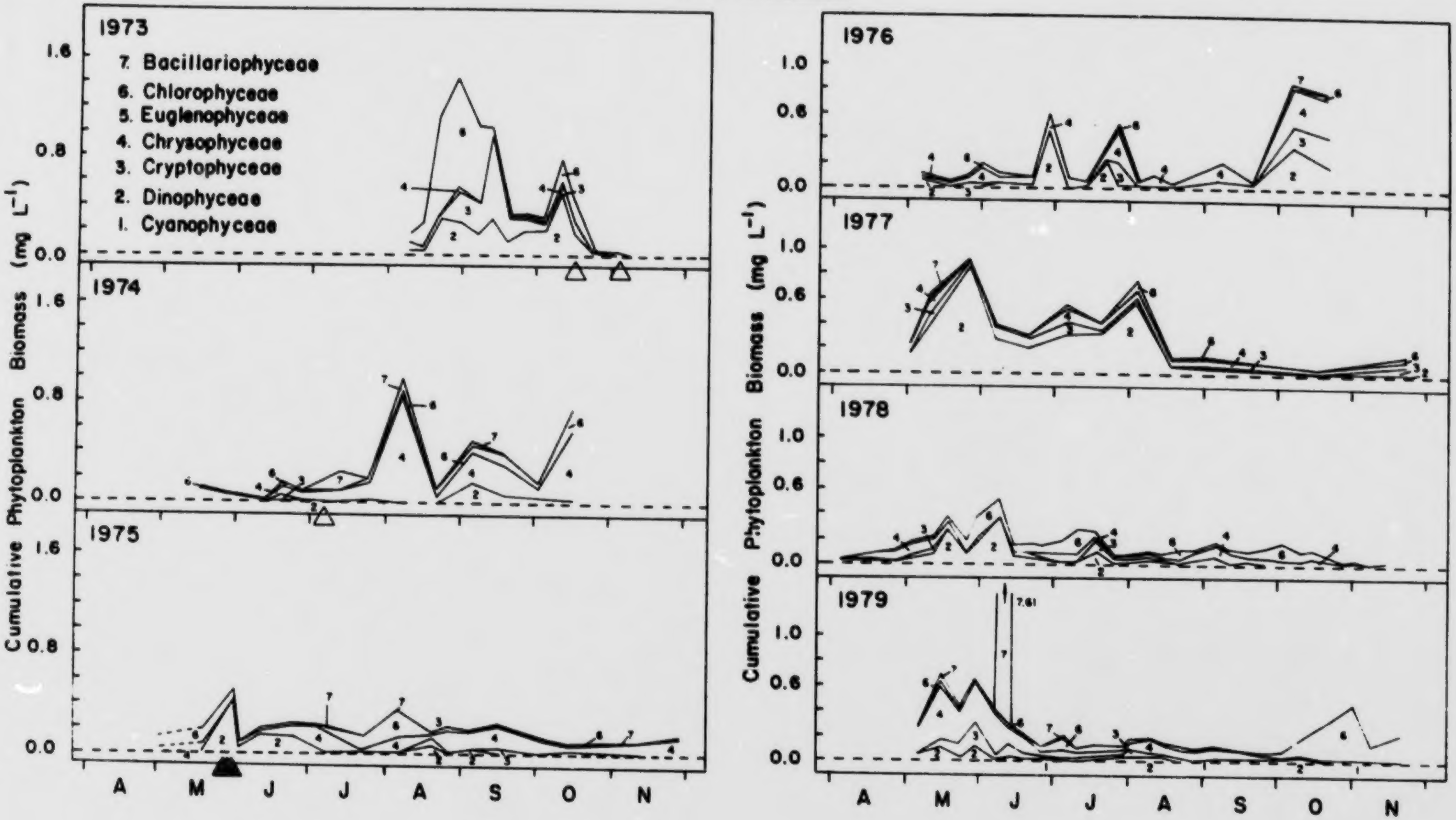


Fig.6-11

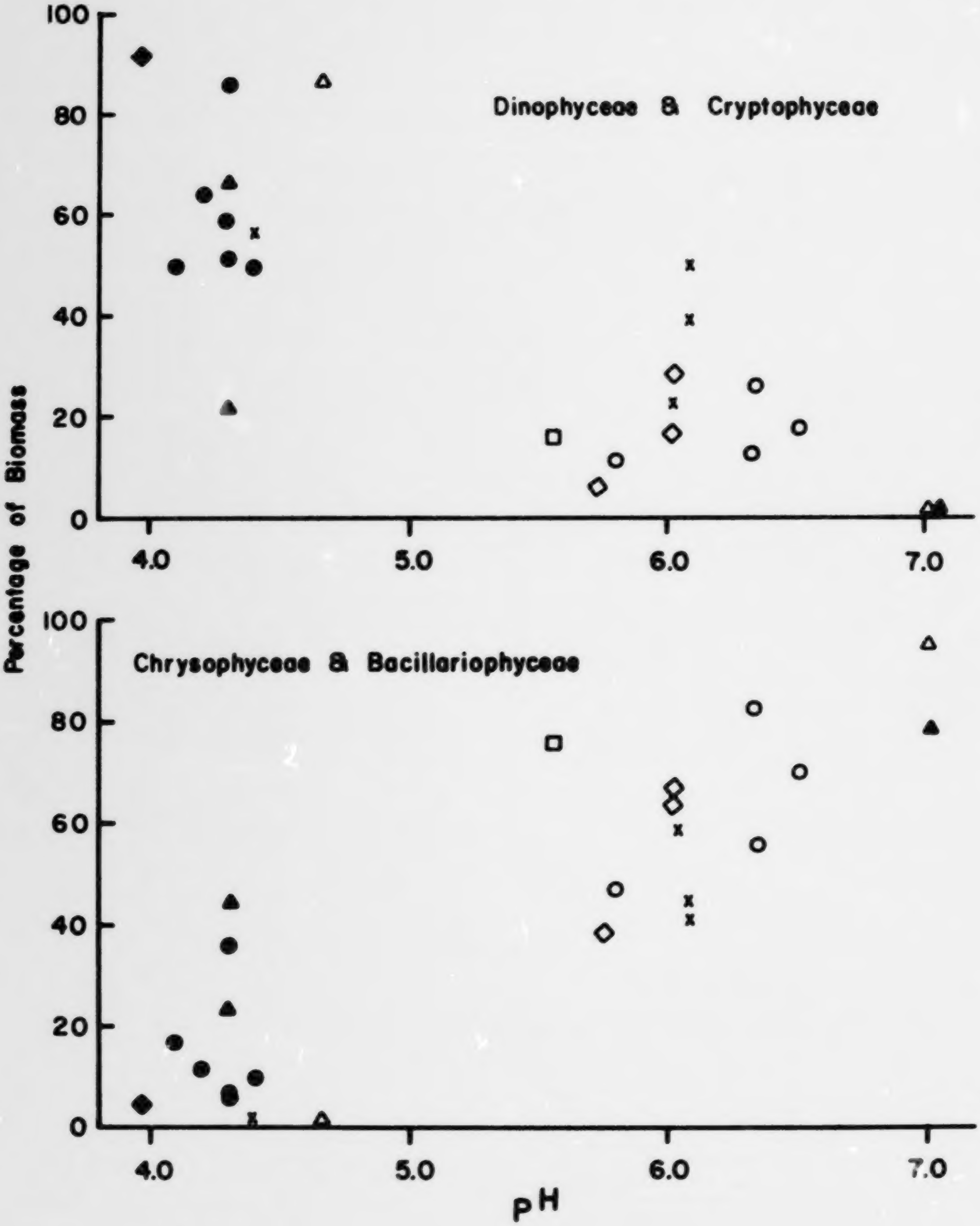

Percentage of Biomass
Dinophyceae & Cryptophyceae
100
80
60
40
20
0
4.0
5.0
6.0
7.0
Chrysophyceae & Bacillariophyceae
100
80
60
40
20
0
4.0
5.0
6.0
7.0
pH

Fig.6-12

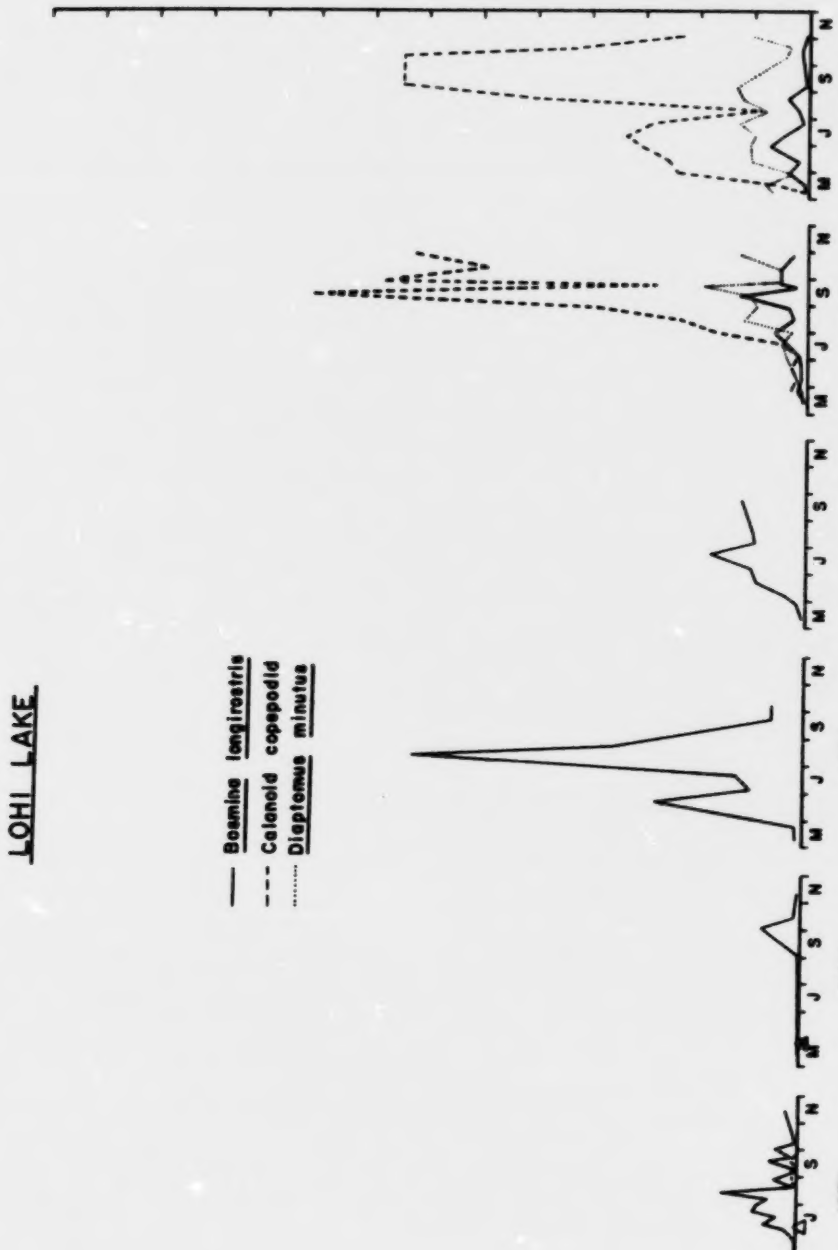
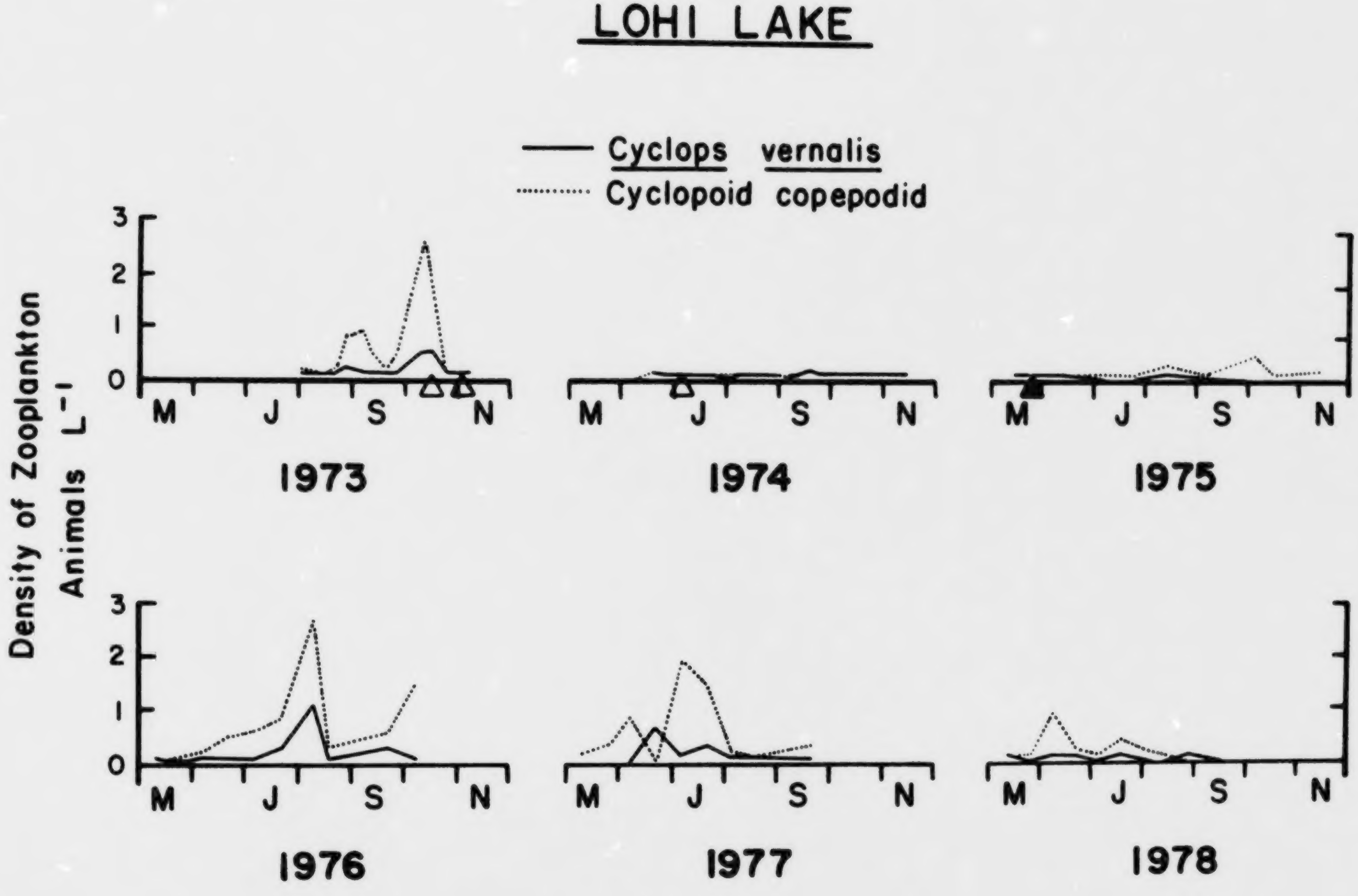

LOHI LAKE
Bosmina longirostris
Calanoid copepodid
Diaptomus minutus
Density of Zooplankton
Animals L⁻¹
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
M
J
S
N
1973
1974
1975
1976
1977
1978
1979

Fig.6-13



LOHI LAKE

CHAPTER 7

EXPERIMENTAL FERTILIZATION OF LAKES NEAR SUDBURY, ONTARIO

N.D. Yan and C. Lafrance

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A. Introduction

Hörnström *et al.* (1973), Almer *et al.* (1978) and Yan (1979) found no correlation between phytoplankton biomass and pH in a comparison of acidic and non-acidic oligotrophic lakes, but did find that phytoplankton biomass and TP were correlated. They suggested that phytoplankton biomass was controlled by supply of TP in acidic as well as in non-acidified lakes, a suggestion which was supported by experiments in which lake pH was experimentally manipulated and changes in phytoplankton monitered (Schindler 1980, Dillon *et al.* 1979). Over the low range of phosphorus concentrations observed in non-enriched Precambrian Shield lakes that are susceptible to acidification (approximately 5-15 $\mu g\ L^{-1}$), relationships between phosphorus and phytoplankton biomass are, however, often poor (Nicholls and Dillon 1978). Any changes in the relationship attributable to acidification would be difficult to detect.

There are reasons to suggest that such differences could exist. Complexation with Al may reduce phosphorus bioavailability in acidic lakes (Almer *et al.* 1978). Turnover times of phosphorus within the water column are generally extremely short in non-acidic, oligotrophic lakes (Rigler 1964), but in acidic lakes they may increase because of reductions in bacterial activities (Laake 1976) or in grazing rates of herbivorous zooplankton (Yan and Strus 1980). These phenomena may result in reduced yields of phytoplankton per unit phosphorus supply in acidic lakes. On the other hand lake transparency increases as lakes acidify (Chapter 1). A consequence of this may be increased productivity in acidified lakes (Schindler 1980).

Much of the existing information on the relationships between nutrients, especially phosphorus, and phytoplankton is attributable to experiments in which the nutrient regimes of entire lakes have been quantitatively manipulated (eg. Schindler and Fee 1974). Such experiments have not been performed in acidified lakes; hence, it is not yet known if acidified and non-acidified lakes differ in their responses to increased rates of nutrient supply.

Fertilization experiments performed in Canadian lakes have also demonstrated that increases in nutrient supply can result in increases in the productivity of communities of zooplankton (Smith 1969, Langford 1950) and fish (LeBrasseur et al. 1978). To determine if responses to fertilization of neutralized, acidified lakes (residually contaminated with trace metals) were similar to those of non-acidic lakes, and to improve the food base prior to introduction of fish, phosphorus was added to Middle Lake between 1975 and 1978 and, for comparison, to Hannah Lake between 1976 and 1978. Scheider et al. (1976b) and Scheider and Dillon (1976) documented that the small changes in concentration of TP produced by fertilization of Middle Lake in 1975 increased chlorophyll levels and shifted dominance of the phytoplankton community from chrysophytes to blue-greens. Dillon et al. (1979) indicated that fertilization of Middle and Hannah Lakes in 1976 with TP resulted in a reduced ratio of total inorganic to total nitrogen (TIN:TN), elevated phytoplankton biomasses and diverse changes in community composition. In this chapter, changes in the chemistry and biota following additions of phosphorus to Middle and Hannah Lakes from 1975 to 1978, are summarized.

To see if acidic and non-acidic lakes differ in their response to high rates of addition of nutrients, i.e. to see if symptoms of eutrophication can develop in acidified lakes, we have fertilized an acidified lake, Mountaintop Lake (pH ~4.6) and a much less acidic lake, Labelle Lake (pH ~6.0), with nitrogen and phosphorus. The effects of these additions on the chemistry and biota of these lakes are described in depth herein. Yan _et al._ (in press) have discussed changes in zooplankton communities in Mountaintop and Labelle Lakes following fertilization.

B. Nutrient Additions and Mass Balances

From July 8 to Sept. 8, 1976, P was added to Mountaintop Lake as a 20:40:0 commercial fertilizer and N as the 20:40:0 and as ammonium nitrate. Phosphorus was added to Mountaintop Lake as 85% technical grade phosphoric acid after Sept. 8, 1976. It was added only as phosphoric acid to Middle, Hannah and Labelle Lakes. In 1977 and 1978, N was added to Mountaintop and Labelle Lakes only,as ammonium nitrate.

The dry fertilizers (20:40:0 and ammonium nitrate) were dissolved in about 130L of water in a 200L drum and poured through a mesh-bottomed bucket over the side of a boat while traversing the lake surface. The phosphoric acid was diluted about 100:1 with lake water and poured slowly over the side of the moving boat.

Quantities of P added to Middle and Hannah Lakes and N and P added to Mountaintop and Labelle Lakes are summarized in Table 7-1. Detailed schedules of nutrient additions are presented in Appendix 1. Loading rates of P were about an order of magnitude higher in Mountaintop and Labelle Lakes than in Middle and Hannah Lakes, as one specific purpose of the fertilization of Mountaintop Lake was to see if acidification would prevent the development of symptoms of eutrophication characteristically observed at high rates of P supply in non-acidic lakes. Schindler _et al._ (1971, 1973) delivered P to Lake 227 in northwestern Ontario at rates about double those of Middle and Hannah Lakes, i.e. (2.85 mg m^{-2} day^{-1} in 1969 and

Table 7-1: Summary of additions of nutrients to S.E.S. lakes. Units are kg N or P with mg m^{-2} day^{-1} in parentheses calculated over the period of fertilization. Detailed addition schedules are listed in Appendix 1.

	1975		1976		1977		1978	
	P[1]	N	P[1]	N[2]	P[1]	N[2]	P[1]	N[2]
Middle	32.3 (1.24)	-	47.9[1] (1.15)	-	34.1 (2.52)	-	53.9 (2.25)	-
Hannah	-	-	35.4 (0.89)	-	15.2 (1.14)	-	36.4 (1.47)	-
Mountaintop	-	-	107 (20.7)	867 (166)	66.6 (17.9)	369 (99)	77.3 (15.8)	631 (129)
Labelle	-	-	-	-	76.7 (16.2)	509 (107)	92.7 (15.2)	602 (98.7)

[1] added as H_3PO_4

[2] added as NH_4NO_3

[3] partially added as 20:40:0 fertilizer

[4] partially added as 20:40:0 fertilizer

3.26 mg m^{-2} day^{-1} from 1970 to 1972).

Ratios of loading of N:P were 6.6:1 and 6.5:1 by weight in Labelle Lake in 1977 and 1978, respectively. Ratios in Mountaintop Lake were 8.1:1, 5.5:1 and 8.2:1 in 1976, 1977 and 1978, respectively. Additions were calculated to immediately raise TP levels of Mountaintop and Labelle Lakes to 100 µg L^{-1} and TIN levels to 1000 µg L^{-1}. Subsequent additions were calculated to maintain these nominal levels; thus, total additions and frequency of additions within each year were variable. In Middle and Hannah Lakes, nominal levels of 10 µg L^{-1} of TP were maintained by phosphoric acid additions in 1975 (Middle Lake only) and 1976, and nominal levels of 15 µg L^{-1} were maintained in 1977 and 1978.

Mass balances of P and N were calculated for the periods of fertilization in Mountaintop and Labelle Lakes. Even though hydrological data were not available for these lakes, the balances were considered to be reasonable estimates as the major source of P and N (additions of fertilizers) could be accurately quantified and as the outflow discharges were very low during most of the fertilization periods. In Middle and Hannah Lakes, measured hydrological data were available for some of the years of fertilization, thereby allowing calculation of relative rates of supply of P from different sources.

The mass of N or P lost to the sediments (S) in Mountaintop and Labelle Lakes was calculated, as in Schindler et al. (1973), as

$$S = J - L_o - \Delta M \qquad (7\text{-}1)$$

where J represents the total supply of P or N to the lake, L_o represents the mass lost through the outlet and ΔM (which was always positive) represents the change in mass of N or P in the lake from the beginning to the end of the fertilization period. The total supply (J) is the sum of the mass exported from the terrestrial portion of the watershed (J_R), the mass deposited from the atmosphere on the lake surface in wet and dry forms (J_p), and the mass added as fertilizers (J_{exp}).

For Mountaintop and Labelle Lakes, J_p was taken from rates of P or N deposition measured at the "Sudbury North" precipitation station (see Chapter 2). For Middle and Hannah Lakes, J_p was taken from the "Sudbury Centre" precipitation station (Chapter 2). The monthly mean deposition rates from January 1976 to December 1979 were used for months with missing data.

Areal unit runoff estimates were calculated for the outlets of Middle, Hannah, Lohi, Clearwater and Nelson Lakes (see Chapter 4). Losses of N or P from Mountaintop and Labelle Lakes (L_o) were calculated as the product of the average unit runoff from these streams, the watershed area of the two lakes and average P or N concentrations in the outlets (where these data were available) or in the lakes (1 m below surface values were used).

The P or N supply attributable to terrestrial runoff (J_R) was calculated differently in Mountaintop and Labelle Lakes than in Middle and Hannah Lakes because of the availability of measured hydrological data for the latter pair of lakes. Scheider _et al_. (1979c) presented water budgets for 6 subwatersheds of Harp Lake, near Huntsville, Ontario. From these data, the fraction of the annual P or N terrestrial export that occurred in months corresponding to the periods of fertilization in Mountaintop and Labelle Lakes was calculated. Scheider and co-workers calculated that 20% and 9.5% of the annual export of P occurred between July and October and between June and August, respectively. Similarly

13% and 1.2% of the annual J_R for N occurred from July to October and from June to August, respectively. For typical Precambrian Shield watersheds, the annual export of N ranges from 80 mg m^{-2} yr^{-1} (Schindler et al. 1973) to 250 mg m^{-2} yr^{-1} (Scheider and Jeffries unpub. data). Dillon and Kirchner (1975) indicated that the range of J_R for P is 0.7 - 8.8 mg m^{-2} yr^{-1} for igneous, forested watersheds. Ranges for the fertilization period of J_R for N and P were, therefore, estimated as fractions (13% or 1.2% for N and 20% or 9.5% for P) of these ranges of annual N or P exports for Mountaintop and Labelle Lakes.

The P input to Hannah Lake from terrestrial runoff for the period June 1977 - December 1978 was calculated using the values measured for Clearwater Inlet 1 (see Appendix 9), prorated by the ratio of the drainage basin areas. Prior to June 1977, a mean monthly input was calculated using the data measured for Clearwater Inlet 1 for the period June 1977 - December 1979 and prorating for watershed area.

Total P is supplied to Middle Lake via terrestrial runoff from the Hannah Lake outlet, Middle Inlet 1 and the ungauged portion of the Middle Lake watershed. Measured input data from the Hannah Lake outlet was available from June 1977 to December 1978 (Appendix 3). Prior to June 1977, a monthly input was calculated as the product of the mean monthly concentration of P in Hannah Lake and the total monthly discharge of the Hannah Lake outlet. Monthly discharge was estimated as follows. In 1978 and 1979, a mean of 55% of the annual precipitation falling on the Hannah Lake watershed contributed to runoff and 45% was lost by evapotranspiration or evaporation (Chapter 4). Using this ratio, the annual runoff was calculated from the annual depth of precipitation which was measured at the Sudbury Airport meteorological station. The mean annual discharge occurring each month was calculated using data from 1978 and 1979, and these ratios were used to calculate total monthly discharges.

The P supplied from Middle Inlet 1 for the period June 1977 - Dec. 1978 was calculated as the product of mean monthly concentration in the stream and total monthly discharge (see Appendix 9). Prior to June 1977, a monthly input was calculated using the mean monthly values measured for Clearwater Inlet 1, prorated for watershed area over the period June 1977 - Dec. 1979. The P input from the ungauged fraction of the Middle Lake watershed was calculated in a manner analogous to that used for the ungauged area of Hannah Lake.

After May of 1977, all external inputs of N (excluding deposition of gaseous species of N) and P into Middle and Hannah Lakes were measured, i.e. J_p (Chapter 2), J_R (Chapter 5) and J_{exp}. Comparisons of measured and predicted monthly average N or P concentrations in the lakes were used to estimate losses of N or P to the atmosphere or to the sediments. Predicted lake water N or P concentrations were determined by dividing the difference between monthly supply rates and monthly outflow loss rates by the lake volume.

C. Results and Discussion - Middle and Hannah Lakes

i. Phosphorus

The major source of TP for Middle and Hannah Lakes was the experimental additions. Excluding potential inputs from dwellings within the lakes' watersheds, fertilization provided 83, 87, 86 and 85% of the P input during the period of fertilization and 63, 68, 57 and 71% of the annual P input to Middle Lake in 1975, 1976, 1977 and

1978, respectively. Similarly, experimental fertilization provided 72, 49 and 70% of the annual P input and 84, 79 and 82% of the P input during the period of fertilization to Hannah Lake in 1976, 1977 and 1978, respectively (Table 7-2). In comparison, about 80% of the annual supply of P to artificially enriched Lake 227 in northwestern Ontario was attributable to fertilization (Schindler *et al*. 1973).

Ice-free period average phosphorus concentrations were not increased by fertilization in Middle Lake in 1975 (7.0 $\mu g\ L^{-1}$) in comparison with previous years (7.1 - 7.3 $\mu g\ L^{-1}$). In all other years of fertilization in Middle and Hannah Lakes, additions of P raised average TP concentrations above pre-fertilization averages. Maximum average concentrations were <15 $\mu g\ L^{-1}$ in the ice-free season in both lakes and were observed in 1976 in Middle Lake and in 1977 in Hannah Lake (Table 7-3). Fluctuations within each year were quite large (Appendix 6).

Phosphorus concentrations were predicted on a monthly basis, as $(J-L_o)/V$, where V was the lake volume, both including and excluding experimentally supplied P. Predicted concentrations were always much greater than measured concentrations in Middle and Hannah Lakes (Fig. 7-1, 7-2). In both lakes, measured TP levels declined slightly from May of 1977 to December of 1979, despite fertilization, indicating that of the fraction of the total supply of P not lost to the outlet more than 100% was lost to the sediments, ie. the concentration of TP in the lake declined. From June of 1977 to December of 1979, the total supply of P to Middle Lake was 134 kg, including fertilization. Only 14% was lost to the outflow. Similarly, only 8% of the P supplied to Hannah Lake was lost to the outflow. Schindler *et al*. (1973) similarly calculated

Table 7-2: Annual supply (J)[1] of P (kg) and supply calculated over period of fertilization only for Middle and Hannah Lakes.

Lake	J	1975 annual	1975 June-Sept.	1976 annual	1976 June-Sept.[2]	1977 annual	1977 July-Sept.	1978 annual	1978 June-Sept.
Middle	J_P	9.73	4.96	10.3	5.35	10.8	2.98	12.5	7.71
	J_R	9.46	1.53	11.8	1.61	15.4	2.59	9.0	1.65
	$J_{Exp.}$		32.3		47.9		34.1		53.9
Hannah	J_P	-	-	9.99	5.48	10.5	2.87	12.1	7.46
	J_R	-	-	4.11	1.09	5.22	1.21	3.38	0.79
	$J_{Exp.}$	-	-		35.4		15.2		36.4

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[1] supply from dwellings in watersheds of Middle and Hannah Lakes are not included. Hannah Lake has 8 permanent dwellings and 3 cottages within its watershed. Middle Lake has 5 permanent dwellings and 7 cottages within its watershed. Assuming that methods presented by Dillon and Rigler (1975) are applicable to Middle and Hannah, the annual phosphorus supply attributable to human activities within the watersheds could equal 29.2 kg P for Hannah Lake and 21.1 kg P for Middle lake.

[2] June to October for Hannah Lake

Table 7-3: Summary of concentrations of TP and nitrogen species ($\mu g\ L^{-1}$) in Middle and Hannah Lakes and ratios of total inorganic to total nitrogen (TIN:TN) and TN to TP. All values are ice-free period averages. Additions of base or P are indicated.

Lake	Year	Treatment	TP	NO_3^--N[3]	NH_4^+-N	Org-N	$\frac{TIN}{TN}$	$\frac{TN}{TP}$
Middle	1973[1]	base	7.3	442	38	142	0.77	85
	1974	-	7.1	417	48	135	0.78	85
	1975	P	7.0	298	28	242	0.57	81
	1976	P	14.6	83	61	307	0.32	31
	1977	P	13.2	94	65	246	0.39	31
	1978	P	10.7	29	49	271	0.22	33
	1979	-	6.0	34	63	184	0.35	47
Hannah	1973	-	8.4	658	25	199	0.77	105
	1974	-	5.7	576	17	133	0.82	127
	1975[2]	base	3.0	524	66	117	0.83	236
	1976	P	11.2	297	64	265	0.58	56
	1977	P	13.9	147	64	298	0.42	37
	1978	P	8.5	92	51	298	0.32	52
	1979	-	7.5	51	44	252	0.27	46

[1] calculated using pre-base addition values only

[2] calculated using post-base addition values only

[3] includes NO_2^--N

that 80% of the P supplied to experimentally fertilized Lake 227 in 1970 and 1971 was retained by the lake, mostly in the sediments.

ii. Nitrogen

Additions of phosphorus resulted in large changes in concentrations of different nitrogen fractions in Middle and Hannah Lakes. Changes in average, ice-free period concentrations of NH_4^+-N from post-neutralization to post-fertilization periods were slight. Levels increased slightly in Middle Lake, but did not change in Hannah Lake (Table 7-3). Nitrate levels declined after fertilization, from 417 μg L^{-1} as N after neutralization in 1974 in Middle Lake, to 29 μg L^{-1} as N in 1978, after four years of additions of P. Similarly, NO_3^--N levels in Hannah Lake were 524 μg L^{-1} in 1975 after base additions, and declined to 92 μg L^{-1} in 1978, the last year of additions of P. Levels of organic N (org-N) increased in both lakes, especially over the first two years of fertilization, suggesting that much of the loss of NO_3^--N was attributable to biological assimilation; however, increases in org-N were less than decreases of NO_3^--N (Table 7-3). Levels of TN, therefore, declined, probably because of sedimentation of org-N (see Chapter 3). The alternative hypothesis that a portion of the NO_3^--N was lost by denitrification (dissimilatory NO_3^- reduction) is unattractive as Middle and Hannah Lakes were never anaerobic (Appendix 5) and denitrification can only occur in a microenvironment that is essentially anaerobic (Keeney 1973).

As a result of decreases in TIN and increases in org-N, ratios of TIN:TN progressively decreased after additions of P. Dillon et al. (1978) similarly observed that loading rates of P to Gravenhurst Bay were negatively correlated with TIN:TN. Despite large decreases in TN, ratios of TN:TP remained >30 (ratios of ice-free period averages), suggesting that on an ice-free period basis, phytoplankton standing stocks were still limited by the supply of phosphorus.

In northwestern Ontario, N, P and C have been added at different rates and in different ratios to several lakes in the Experimental Lakes Area (Schindler and Fee 1974). Only P was added to Lake 261 and concentrations of P, calculated over the ice-free season, increased from 12-16 μg L^{-1}, prior to fertilization (1971 and 1972), to 20-24 μg L^{-1} from 1973 to 1976. Average levels of NO_3^--N and NH_4^+-N were low prior to additions of P and did not change after additions. Levels of org-N, in contrast, increased from 275-317 μg L^{-1}, prior to additions of P, to 360-548 μg L^{-1} after additions (Table 7-4). The increase in org-N occurred without an increase in densities of nitrogen fixing blue-green algae (Findlay 1978). In Middle and Hannah Lakes and in Lake 261 org-N levels increased, but this increase accompanied decreases in TN in Middle and Hannah Lakes,while in Lake 261 TN levels increased. This difference between the two studies is a reflection only of the pre-fertilization availability of NO_3.

Rapid changes in levels of NO_3^- and NH_4^+ occurred within, as well as between years indicating concentrations were primarily controlled by biological, not hydrological, phenomena. In Hannah Lake, NO_3^--N (Fig. 7-3) and NH_4^+-N (Fig. 7-4) concentrations showed little seasonal variation prior to manipulation. In 1975, after additions of base, levels of NH_4^+-N increased from ~30 μg L^{-1} in June to 80 μg L^{-1} in October. Levels of NO_3^--N decreased over the same period. From 1976 to 1979, peak concentrations of NH_4^+-N occurred within a few weeks of the disappearance of ice in the spring.

Table 7-4: Ice-free period concentrations ($\mu g\ L^{-1}$) of N and P in Lake 261 in northwestern Ontario from 1973 to 1976. Yearly averages are averages of monthly means corrected for morphometry from Schindler (unpublished data). Phosphorus was added to Lake 261 at a rate of 0.246 g $m^{-2}\ yr^{-1}$ from 1973 to 1976 inclusive.

	N or P Concentration					
	1971	1972	1973	1974	1975	1976
NO_3^--N	5.6	10.2	6.0	2.6	7.8	12.9
NH_4^+-N	20.6	33.2	29.6	23.8	30.5	28.0
org-N	317	275	360	412	380	548
TN	343	319	396	438	418	589
TP	16.1	12.2	19.9	23.4	23.2	24.4

Levels subsequently declined, and additions of P accelerated the rate of decline (Fig. 7-4). Fluctuations in NH_4^+-N levels were similar in Middle Lake. Levels were highest in the early spring and rapidly declined to low summer levels, especially after fertilization (Fig. 7-5).

Changes in measured NO_3^--N and NH_4^+-N levels over the summer and winter periods are indicated in Table 7-5. Also indicated are predicted changes calculated on a monthly basis as $(J-L_0)/V$. The calculation assumes no biological transformation, no gaseous inputs or losses of N, and no internal loading or losses of N. Although these assumptions are false, differences between measured and predicted concentration changes facilitate estimations of the magnitude and kinds of biologically-mediated nitrogen transformations, assuming gaseous inputs and losses of N are comparatively small.

Predicted NH_4^+-N levels increased over the summer in all years in Middle and Hannah Lakes (Table 7-5). In actuality, substantial decreases in NH_4^+-N occurred, attributable to assimilation by the phytoplankton and/or to nitrification. Measured increases in NH_4^+-N levels over the winter period were generally much greater than predicted increases. NH_4^+-N is most likely being generated by hydrolytic decomposition of organic matter under oxygenated conditions.

In both Middle and Hannah Lakes, NO_3^--N levels did not vary over the ice-free season prior to neutralization. Levels were slightly reduced by additions of base, but the largest reductions followed additions of phosphorus. Similar to NH_4^+-N, NO_3^--N levels were highest in the spring. In Hannah Lake, spring NO_3^--N levels declined each year from 1976 to 1979

Table 7-5: Comparison of measured $NO_2^-+NO_3^-$ and NH_4^+ levels with levels calculated assuming concentrations are the product of physical processes only. All concentrations are as μg N L^{-1}. Calculation method is described in text. "Initial" concentrations were measured at the beginning of the stated time interval. "Predicted" and "Measured" concentrations are for the end of the stated time interval.

Lake	Species	[N]	June- Aug. 1977	Aug. 1977- May 1978	May- Aug. 1978	Aug. 1978- May 1979	May- Sept. 1979
Hannah	$NO_2^-+NO_3^-$	initial	260	10	250	5	150
		predicted	286	118	283	95	175
		measured	30	235	5	150	5
	NH_4^+	initial	100	15	165	20	100
		predicted	132	92	195	68	122
		measured	10	165	20	100	20
Middle	$NO_2^-+NO_3^-$	initial	180	10	85	5	90
		predicted	197	119	113	149	107
		measured	10	85	5	90	5
	NH_4^+	initial	100	40	92	20	150
		predicted	131	91	111	58	154
		measured	40	92	20	150	114

(Fig. 7-3). The duration of time at which levels were at a minimum increased each year. By 1979, in fact, levels were below analytical detection limits (5 μg L^{-1}) for most of July and August. Seasonal patterns of NO_3^--N in Middle Lake (Fig. 7-6) were similar to those of Hannah Lake. By 1979 levels were usually <5 μg L^{-1} in July, August and September. Depletion of NO_3^--N in epilimnetic waters to <5 μg L^{-1} is characteristic of Precambrian lakes in central Ontario (see Table 1-8) and lakes in northwestern Ontario (Armstrong and Schindler 1971).

Similar to NH_4^+-N, predicted NO_3^--N levels at the end of the summer vastly overestimated measured levels (Table 7-5), indicating uptake and reduction of NO_3^- by the biota.

iii. Metals and Major Ions

Fertilization had little affect on concentrations of trace metals. Cu, Ni and Al concentrations declined from spring to autumn in Middle and Hannah Lakes during years when phosphorus was added. Declines of similar magnitude also occurred in unfertilized Lohi Lake prior to its re-acidification in 1976, but did not occur from 1977 to 1979, after the re-acidification of the lake. Neutralization substantially reduced the proportion of Cu and Zn existing in "labile" forms (determined by anodic stripping voltometry). This proportion was not further reduced by fertilization, suggesting that inorganic ions, not organic materials, were the primary complexing agents in Middle and Hannah Lakes. Prior to fertilization, but after neutralization in Hannah Lake in 1975, for example, 22% of the total unfiltered Cu (t-Cu) and 58% of t-Zn were labile (Appendix A-6). These percentages were similar to those measured in Lohi Lake in 1976 (24% for Cu and 50% for Zn) after neutralization. The percentages after fertilization in Hannah Lake (average of 3 years) were not different from these pre-fertilization levels (23% for Cu and 45% for Zn). Pagenkopf et al. (1974) indicated that copper was highly complexed by carbonate and hydroxide in natural waters. Thus, a change from pH ~4.5 to ~7.0 should substantially reduce proportions of Cu^{++}, a component of the labile copper. Complexation with organic matter becomes important at concentrations of organic material higher than that observed in the fertilized lakes (Wilson 1978).

Schindler et al. (1971) noted that fertilization of Lake 227, in northwestern Ontario, produced no changes in major ions other than increases in Na^+ levels attributable to additions of N as $NaNO_3$. There were major changes in Na^+, Cl^-, Ca^{2+} and SO_4^{2-} levels between 1973 and 1979 in Middle and Hannah Lakes, but these changes were not attributable to additions of P (see Chapter 8). Changes in Ca^{2+} were attributable in part to the initial additions and subsequent depletions of $Ca(OH)_2$ and $CaCO_3$. While the alkalinity of Lohi Lake decreased steadily after the final addition of base in 1975, the alkalinity of Middle and Hannah Lakes increased. Prior to fertilization, NO_3^--N levels were about an order of magnitude higher than levels of NH_4^+-N. Fertilization resulted in decreases in NO_3^- because of biological NO_3^- reduction, an alkalinity-generating process (Brewer and Goldman 1976). Amounts of alkalinity that were generated are quantified in Chapter 8.

iv. Phytoplankton

a. Phytoplankton Biomass

Fertilization resulted in increases in phytoplankton biomass in Middle and Hannah Lakes. Averaged over the ice-free season, biomass varied from 0.52 to 0.93 mg L^{-1} in the 4 years of fertilization in Middle Lake, higher than the 0.46 mg L^{-1} observed prior to neutralization. Similarly, from 1976 to 1978 in Hannah Lake, biomass varied from 0.50 to 1.63 mg L^{-1}. Prior to neutralization, yearly averages were 0.26 and 0.34 mg L^{-1} (Appendix 7).

Including data (averages over the ice-free season) from all SES lakes, with the exception of Mountaintop and Labelle Lakes which had much higher concentrations of TP, phytoplankton biomass (in mg L^{-1}) was related to TP (in µg L^{-1}) by the regression equation

$$\text{Biomass} = 0.090\ \text{TP} - 0.112 \qquad (7\text{-}2)$$

This relationship was significant ($r^2 = 0.42$, $p < 0.01$), but biomass was not correlated with pH ($r^2 = 0.005$, Fig. 7-7). The slope of the regression equation was less than that determined by Schindler et al. (1978) for experimentally fertilized lakes in northwestern Ontario (Biomass = 0.32TP - 1.7) and also less than observed by Nicholls and Dillon (1978) for a set of lakes in the Kawartha Lake - Trent River system in southern Ontario (Biomass = 0.21 TP). The reduced slope in the regression equation in the SES lakes might indicate that the residual contamination of the lakes with metals restricted the response of the phytoplankton to nutrient additions. It is, however, difficult to compare studies where the range of the independent variable (TP) varied from 3-15 µg L^{-1} (SES data) to 5-40 µg L^{-1} (Schindler et al. 1978) to 5-75 µg L^{-1} (Nicholls and Dillon 1978). Extracting fractions of the ELA and southern Ontario data with TP levels comparable to Fig. 7-7, would have produced equations with different slopes than those reported for the complete sets of data.

The correlation between phytoplankton biomass and TP in the SES data appears as good as that in the ELA and southern Ontario when TP levels >15μg L^{-1} were eliminated. This was so despite the previous contamination (H^+ and metals) and previous manipulation (neutralization) of some of the SES lakes. Nevertheless 58% of the variance in biomass data in the SES lakes was not explicable by TP. Several other sources of variance existed. There were problems of analytical precision at low levels of TP, especially in the early years of the study (see TP levels in Clearwater Lake, Appendix 6). Some of the unexplained variance might have been attributable to the inherent response time of the phytoplankton communities to changes in rates of supply of TP, or to changes in pH (post-neutralization recovery times). Thirdly, some of the variance might have been attributable to the influence of changes in N:P ratios on phosphorus-biomass relationships (Smith and Shapiro 1980). N:P ratios did change substantially over the total period of fertilization, and N most likely became limiting in the summer of 1978. Levels of NO_3^--N were <5 μg L^{-1} from August 3 to October 2, 1978, in Hannah Lake and from June 26 to September 18 in Middle Lake. Over these periods of time, TIN/TP ratios were 3.1:1 for Hannah Lake and 3.5:1 for Middle Lake.

The significant positive correlation between phytoplankton biomass and TP over the small range of TP levels indicates that while the residual contamination of Middle and Hannah Lakes with metals might have had some effect, phytoplankton standing stocks were still controlled by the supply of phosphorus.

b. Phytoplankton Community Structure

Relative contributions of the different algal classes to total biomass in Hannah and Middle Lakes are summarized in Fig. 7-8 and 7-9, respectively. Dominant genera, or species, are indicated in Fig. 7-10 (Hannah Lake) and Fig. 7-11 (Middle Lake). Dinoflagellates, especially Peridinium inconspicuum Lemmermann, were the dominant phytoplankters in both lakes in 1973, prior to manipulations. In Hannah Lake, chrysophytes, in the spring only, and green algae and diatoms, in addition to dinoflagellates, were important contributors to total biomass in 1974. Dominance by diatoms is very unusual for extremely acidic lakes such as Hannah Lake (Chapter 1).

Additions of base in the fall of 1973 to Middle Lake and in the spring of 1975 to Hannah Lake resulted in a change in dominance from dinoflagellates to chrysophytes in both lakes, without any long-term change in biomass. Thus, prior to additions of P, chrysophytes formed virtually all of the biomass in both lakes (Fig. 7-8 and 7-9). After additions of P, as before, chrysophytes were the dominant class of algae in the spring in Middle and Hannah Lakes. A spring dominance by chrysophytes is typical of Precambrian Shield lakes in general, and is also commonly observed in experimentally fertilized lakes in northwestern Ontario (Schindler et al. 1973). Chrysophytes may also be important in the winter in eutrophic lakes. Nicholls (1976b), for example, did not observe chrysophytes in the Holland Marsh from June to November of 1971, but they formed 26% of the biomass from December to March. Chrysophytes were also dominant in the late fall in Hannah Lake in each year of fertilization (Fig. 7-8) and in the late autumn of 1975 and 1976 in Middle Lake (Fig. 7-9).

While spring phytoplankton assemblages were predictably chrysophyte-dominated, dominance of summer and fall assemblages was variable. In Middle Lake in 1975, blue-green algae became dominant in the summer and fall after additions of P. The dominant taxon was Oscillatoria (Fig. 7-11), which had been previously identified (Dillon et al. 1979) as a Mastigocladus sp. Except for a short time when blue-greens were dominant, green algae were most commonly dominant in the summer in 1976, with diatoms and chrysophytes replacing them in the fall. In 1977, fertilization of Middle Lake began in July and green algae and diatoms immediately replaced chrysophytes as dominants. Cryptomonads and diatoms were the most important classes in the fall of 1977 in Middle Lake and, except for one period of time in late September, they were also dominant in 1978. In summary, at different times over the four years of fertilization in Middle Lake, blue-green and green algae, diatoms and cryptomonads were dominant (Fig. 7-9, 7-11).

The responses of phytoplankton in Hannah Lake were not the same as in Middle Lake. In 1976, additions of P increased phytoplankton biomass, but while the biomass of green algae increased, chrysophytes remained dominant. In 1977, as in the same year in Middle Lake, greens and diatoms were the dominant phytoplankters in the summer. In 1978, seasonal succession patterns were quite complex with greens, diatoms, then dinoflagellates becoming sequentially dominant between June and September and chrysophytes re-assuming dominance in October and November.

Some of the responses that occurred in Middle and Hannah Lakes have been observed in previous whole-lake fertilization experiments in Canada. The stimulation of the blue-green Oscillatoria in Middle Lake in 1975 is reminiscent of Crecy Lake in New Brunswick, where blue-greens were the dominant phytoplankters stimulated by additions of N and P (Smith 1969). Green algae were stimulated by fertilization in some years in both Middle and Hannah

Lakes. Findlay (1978) noted that greens were the most common dominant phytoplankters in Lake 227 after fertilization. Cryptomonads assumed dominance in the latter portion of 1977, and in 1978, after additions of P in Middle Lake. Cryptomonads are often dominant in the fall in fertilized lakes (Findlay 1978), and they may be dominant during all seasons in eutrophic lakes (Granberg 1973).

Langford (1950) and Parsons _et_ _al_. (1972) have noted increases in diatom flora accompanying fertilization of lakes. The highest biomasses observed in Middle and Hannah Lakes were attributable to diatoms. In Middle Lake, the biomass of _Synedra radians_ reached 3.2 mg L^{-1} and _Fragilaria_ sp. reached 2.4 mg L^{-1} on October 6, 1976. Hutchinson (1967) considers both taxa to be indicative of enriched conditions. _Synedra_ sp. and _Rhizosolenia_ sp. together accounted for a biomass of 4.2 mg L^{-1} at their maximum densities in Hannah Lake in 1976. _Rhizosolenia_, was also important at times in Middle Lake, with peak standing stocks of 3.1 mg L^{-1} in July and 0.9 mg L^{-1} in October of 1977.

The phytoplankton community of Hannah Lake in 1976 was exceptional in that chrysophytes remained as community dominants after fertilization. The supply rates of P in fertilizer were lower in this year in Hannah Lake than in any other year in the two fertilized lakes. The low rate of supply is the most likely reason that the community structure did not change. Changes in phytoplankton populations following additions of C and/or N and/or P to lakes in northwestern Ontario are described by Findlay and Kling (1975) and Findlay (1978). Loading rates of P to Lakes 304 (1975 and 1976 only), 227, 226 North and 261 decreased from 1.0 to 0.5 to 0.34 to 0.25 g m^{-2} yr^{-1}, respectively. Dominant taxa were blue-greens in 226N and greens, with blue-greens, cryptomonads and occasionally dinoflagellates in Lakes 227 and 304; however, as in Hannah Lake in 1976, chrysophytes remained as the common summer dominants in Lake 261, the lake with the lowest loading rates of P.

Schindler (1975) has observed that despite his very precise quantification of nutrient input rates, lake physics and chemistry in ELA lakes, phytoplankton responses to nutrient additions incorporating taxonomic detail could not be predicted. The responses to fertilization in Middle and Hannah Lakes were very complex and variable both within and between years. It is apparent, however, that small increases in loading rates of P produced measurable increases in biomass without changes in community structure (Hannah Lake 1976). Slightly larger increases in rates of supply of P produced complete changes in community structure.

v. Zooplankton

a. Crustacean Zooplankton Biomass

In Sweden, zooplankton communities of acidified lakes recovered from neutralization far more slowly than phytoplankton communities (Bengtsson *et al.* 1980). Similarly, in Lohi Lake zooplankton community structure that is typical of non-acidic lakes had not been re-established by 1977, the year that residual alkalinity was exhausted, 4 years after the initial additions of base. Phytoplankton community structure that was typical of non-acidic lakes had reappeared much earlier. Zooplankton abundances in Lohi Lake increased in 1976 and 1977 from low post-neutralization levels, but they did not equal pre-neutralization levels, which were similar to abundances in non-acidic lakes, until 1978, 5 years after the additions of base. Fertilization of Middle and Hannah Lakes, therefore, began well before the lakes' zooplankton communities would have completely recovered from additions of base.

In Hannah Lake, fertilization was accompanied by an increase in the biomass of planktonic crustacea. Levels greatly exceeded those observed prior to neutralization. The maximum average biomass was 24.1 mg m^{-3} in 1976 (Table 7-6). (Rotifer biomass increased this number by only 3% . The dominant rotifer was Anuraeopsis fissa.) From 1977 to 1979, zooplankton densities and biomasses were again much higher than before neutralization (Table 7-6), but even at their highest (1976), the value was lower than that of unfertilized Nelson Lake (34-46 mg m^{-3}, Table 6-17), lower than the range in biomass of 26 - 49 mg m^{-3} observed by Yan and Strus (1980) in oligotrophic lakes in central Ontario and much lower than that observed by Malley (1981) in non-acidic lakes in northwestern Ontario that were artificially enriched.

In Middle Lake, zooplankton biomass did not increase in the first year of fertilization (1975), but it increased to pre-neutralization levels in 1976 and maintained these levels until 1978 (Table 7-6). In comparison with Lohi Lake which was neutralized but not fertilized, fertilization changed the magnitude, but not the timing of changes in biomass. Biomass increased to pre-neutralization levels in Middle Lake (Table 7-6), but not in Lohi Lake two years after neutralization.

In both Middle and Hannah Lakes, biomass fell in 1979 (Table 7-6). The increase in biomass the year of, or one year after fertilization, and the immediate decrease in biomass accompanying the cessation of fertilization is a more rapid response than that following fertilization of Crecy Lake in New Brunswick. In that lake, Smith (1969) observed increases in zooplankton densities which

Table 7-6: Summary of crustacean zooplankton data from Middle and Hannah Lakes, 1973-1979. 1973 data from Middle Lake and 1975 data from Hannah Lake are pre- and post-neutralization data, respectively. Appendix 8 presents data in greater detail.

		Number of Species		Density (animals L^{-1})		Biomass (mg m^{-3})		Percent Biomass					
Lake	Year	yr^{-1}	collection^{-1}	mean	range	mean	range	*B. longirostris*	*C. sphaericus*	Other Cladocera	Nauplii	Calanoida	Cyclopoida
Middle	1973	6	3.4	19.7	0.4 -76	13.7	0.1 -53	92.0	0.4	0.1	6.3	0	1.2
	1974	5	2.7	0.56	0.02-2.7	0.88	0.01-6.0	20.5	3.0	0	0.2	9.0	67.3
	1975	6	3.0	1.28	0.04-6.6	0.9	0.03-5.5	1.8	22.7	0	26.2	0.1	49.2
	1976	4	2.8	26.1	0.6 -118	16.3	0.4 -74	0.1	96.8	0	1.2	<0.1	1.9
	1977	6	3.1	14.2	0.7 -35	12.8	0.3 -42	<0.1	16.3	1.3	18.1	0.1	64.2
	1978	5	2.8	14.3	0.1 -41	19.0	0.1 -62	<0.1	3.7	0.4	7.0	0	88.8
	1979	6	4.0	3.22	0.9 -11	4.3	0.7 -16	4.2	7.8	1.3	7.6	0.9	78.2
Hannah	1973	5	2.9	1.1	0.06-3.1	0.68	0.05-2.2	59.6	10.9	0.4	24.8	0	4.3
	1974	5	3.1	0.64	0.03-4.3	0.71	0.02-5.2	34.8	7.5	0	0.3	23.9	33.5
	1975	3	2.4	0.15	0.02-0.44	0.07	0.03-0.26	3.3	20.4	0	50.4	0	25.9
	1976	5	2.7	55.4	0.9 -289	23.6	0.4 -145	<0.1	6.3	<0.1	71.5	<0.1	22.1
	1977	4	2.5	8.7	0.2 -23	5.29	0.1 -16	0	51.0	1.2	17.8	0	30.0
	1978	8	3.1	23.5	0.2 -64	13.6	0.1-41.8	<0.1	7.3	0.8	32.8	0.9	58.2
	1979	8	3.8	5.4	0.5 -12	4.06	0.5 -10	1.8	12.7	1.6	9.6	2.0	72.3

began 2 years after fertilization and lasted between 2 and 3 years.

b. Zooplankton Community Structure

Fertilization did not result in increases in the average richness of species (average number of species observed per collection); however, total numbers of species reported per year increased in 1978 and 1979 in Hannah Lake (Table 7-6). *Tropocyclops prasinus mexicanus* Kiefer, *Diaphanosoma leuchtenbergianum* *Fisher and *Diaptomus oregonensis* Lilljeborg occurred for the first time in 1978. *Daphnia retrocurva* Forbes, *D. galeata* Sars *mendotae* Birge, and *Eucyclops agilis* Koch were observed for the first time in 1979. *Diaptomus minutus* Lilljeborg occurred frequently for the first time in 1979 (Appendix 8). The appearance of new species, especially *Daphnia*, indicates that the zooplankton community of Hannah Lake, was recovering from acidification by 1978 and 1979. Many of these species have not yet been reported from Middle Lake, but their occurrence in the upstream lake will speed their invasion of Middle Lake. Reappearance, however, does not guarantee successful re-establishment of the species. Rates of reappearance of species should not be generalized to neutralized acidic lakes that do not have associated metal problems.

Simocephalus serrulatus Koch was an important cladoceran in Middle and Hannah Lakes in 1979, but at all other times *Bosmina longirostris* O.F. Muller and *Chydorus sphaericus* O.F. Muller were the only numerically important Cladocera (Table 7-6, Fig. 7-12 and 7-13). Brooks (1969) observed that *C. sphaericus* is one of the few zooplankton that can ingest blue-green algae and, in consequence, it

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*Some specimens were indistinguishable from *D. brachyurum* Lieven.

frequently increases in abundance in eutrophic lakes during blooms of blue-greens. In Middle Lake, C. sphaericus did replace B. longirostris in the fall of 1975 (Fig. 7-13), at a time when most of the phytoplankton biomass, in fact, was contributed by the blue-green alga, Oscillatoria (Fig. 7-8). However, densities of C. sphaericus did not reach a maximum until 1976, when they formed 97% of the zooplankton biomass (Table 7-6). In 1976, blue-green algae were not important phytoplankters in Middle Lake. In Hannah Lake, C. sphaericus replaced B. longirostris after neutralization (1975), but did not reach maximum biomass until after fertilization (Fig. 7-10).

Among copepods, calanoids were unimportant in Middle and Hannah Lakes prior to neutralization, and neutralization and fertilization did not increase their importance. Fertilization stimulated cyclopoids from 1977 to 1979 in Middle Lake and from 1976 to 1979 in Hannah Lake (Table 7-6). Cyclops vernalis Fischer was the dominant cyclopoid in Hannah Lake. In Middle Lake, C. vernalis was the only cyclopoid of importance in 1977, and along with Orthocyclops modestus Herrick, was important in 1978 (Fig. 7-14) and 1979.

C. vernalis is probably the most acid- and metal- tolerant of the cyclopoid copepods indigenous to the Precambrian Shield. It was the dominant cyclopoid in Middle, Hannah, Lohi and Clearwater Lakes prior to manipulations (see Chapter 1). Carter et al. (1980) noted that C. vernalis occurred frequently in lakes in eastern North America (29% of 696 lakes). Its occurrence was independent of variables such as Secchi disc transparency, that are well correlated with nutrient load. Nevertheless, Patalas (1972) and Watson and Carpenter (1974) noted that C. vernalis reached maximum densities in the most eutrophic waters of the Great Lakes, namely the western basin of Lake Erie. Keller (1981) similarly noted that in a survey of 187 lakes in the Sudbury area C. vernalis occurred in the most acidic lakes (pH ~4.5), but reached maximum relative densities in the most enriched lakes. While the original presence of C. vernalis in Middle and Hannah Lakes indicates highly evolved mechanisms of acid- and metal- tolerance, increases in abundance of this species may indicate a response typical of nutrient enrichment. This increase occurred, however, at community biomasses less than those typically observed in oligotrophic lakes.

Levels of Cu varied from 43 - 117 $\mu g\ L^{-1}$ on average in Middle Lake and from 45 - 52 $\mu g\ L^{-1}$ in Hannah Lake during the years of fertilization. Toxicological studies indicate that such levels might restrict the response of crustacean zooplankton to fertilization. Winner and Farrel (1976) noted that 40 - 80 $\mu g\ L^{-1}$ of Cu reduced instantaneous rates of population growth of 4 species of Daphnia. Biesinger and Christensen (1972) observed that the rate of production of young by Daphnia magna was reduced 16% at 22 $\mu g\ L^{-1}$ of Cu and 50% at 35 $\mu g\ L^{-1}$ of Cu in three week experiments in Lake Superior water. Both of these investigations were performed in water of much higher alkalinity than in Middle and Hannah Lakes.

Other metals were present in Middle and Hannah Lakes at potentially toxic concentrations. Ni levels ranged from 300 - 500 $\mu g\ L^{-1}$ after fertilization (Table 6-3), much higher than the concentration that Biesinger and Christensen (1972) noted would reduce production of Daphnia magna offspring by 50% (95 $\mu g\ L^{-1}$). Pb, Zn, Mn and Al were also present in the lakes. As Borgmann (1980) indicated that the toxicity of mixtures of trace metals is at least additive and often synergistic, it appears that metal toxicity prevented the development of higher zooplankton biomasses following fertilization in Middle and Hannah Lakes.

D. Results and Discussion - Mountaintop and Labelle Lakes

i. Temperature and Oxygen

Fertilization of Labelle Lake resulted in a 1 m reduction in the thickness of the epilimnion. In Mountaintop Lake, fertilization was accompanied by a larger decrease (2 to 4 m) in the thickness of the epilimnion (Fig. 7-15) and a substantial decrease in hypolimnetic temperatures (Fig. 7-16), resulting in later autumnal overturns (Fig. 7-15). The changes in thermal regime in Mountaintop Lake were attributable to the decrease in transparency that accompanied fertilization (Fig. 7-17), since there were no significant differences among years taken in pairs in either average wind speed or amount of sunshine ($p > 0.05$ for t-tests between years pairing months). From May to October, average wind speeds were 18.8, 18.7 and 18.0 km hr^{-1} and average number of hours of bright sunshine were 195, 223 and 226 $month^{-1}$ in 1976, 1977 and 1978, respectively.

It was evident from oxygen profiles that Mountaintop Lake did not experience complete spring overturns from 1977 to 1979. Oxygen profiles were orthograde in May of 1976, indicating that spring overturn had been complete in that year (Fig. 7-18). Spring overturn was not complete in Labelle Lake in all three years of study (Fig. 7-19). Incomplete spring mixing is commonly observed in well protected, small Shield lakes. Summer oxygen profiles were positive heterograde from 1977 to 1979 in both lakes. Deep hypolimnetic waters were anoxic for long periods of time in Labelle Lake in all years (Fig. 7-19). In Mountaintop Lake, the profundal waters were well-oxygenated in 1976, but were anoxic in late August of 1977, from May to August of 1978 and for the summer of 1979 (Fig. 7-18).

ii. Metals

Average concentrations of several metals in Mountaintop and Labelle Lakes are shown in Table 7-7. The source of these metals is discussed in Chapters 1, 2 and 3. Levels of Ni were approximately 10 μg L^{-1} in both lakes and were not affected by fertilization. Levels of Cu were initially greater in Mountaintop Lake than in Labelle Lake. This difference could have been due to a large input of Cu in acidic spring melt-water in Mountaintop Lake. The most likely cause for Cu reductions in Mountaintop Lake was biological uptake followed by sedimentation of the Cu in a bound form. Al and Mn levels were greatly elevated in Mountaintop Lake, as is typical of acidified lakes. Levels were not greatly affected by fertilization, even though the profundal waters were frequently virtually anoxic after 1977. Concentrations of Fe increased through time in both lakes (Table 7-7 and Appendix 6) probably because of return of Fe from the sediments when profundal waters were anoxic (Fig. 7-20).

iii. Phosphorus and Nitrogen

The average concentration of TP in Mountaintop Lake was 6.5 μg L^{-1} prior to fertilization in 1976. Average concentrations in the post-fertilization portions of the ice-free season increased to 58, 66 and 82 μg L^{-1} after additions of P in 1976, 1977 and 1978, respectively (Table 7-8). Maximum levels were >100 μg L^{-1} in each year, and they were reached earlier in the season in successive years of fertilization. Spring concentrations increased to 19 μg L^{-1} in 1977 and to 28 μg L^{-1} in 1978 (Fig. 7-21), indicating

Table 7-7. Ice-free period averages ($\mu g\ L^{-1}$) of metal concentrations in Mountaintop and Labelle Lakes. (For ranges of values see Appendix 6).

Lake	Year	Al	Mn	Fe	Cu	Ni
Mountaintop	1976 pre-fertilization	440	120	215	24	12
	post-fertilization	282	108	107	6	11
	1977	293	105	234	4	12
	1978	310	118	514	3	10
	1979	366	106	856	3	11
Labelle	1977 pre-fertilization	73	75	73	5	13
	post-fertilization	29	51	59	3	9
	1978	97	174	181	4	19
	1979	59	135	145	2	10

Table 7-8. Average concentrations of N and P in Mountaintop and Labelle Lakes calculated for the post-fertilization portions of the ice-free periods of 1976 to 1978.

	Mountaintop			Labelle	
	1976	1977	1978	1977	1978
TP ($\mu g\ L^{-1}$)	58	66	82	64	68
TIN ($\mu g\ L^{-1}$)	1392	778	694	776	775
org-N ($\mu g\ L^{-1}$)	445	433	436	450	560
org-N/TN	0.24	0.36	0.39	0.37	0.42
TN/TP	31.7	18.4	13.8	19.2	19.6

that most, but not all of the P was lost from the water column during the autumn and winter.

The concentration of TP prior to fertilization in 1977 in Labelle Lake was 11 $\mu g\ L^{-1}$. Comparable levels of 12 $\mu g\ L^{-1}$ and 14 $\mu g\ L^{-1}$ were observed in the pre-fertilization period of 1978 and in April 1979, respectively, indicating rapid sedimentation of added P. Average concentrations were quite similar in both years after fertilization, 64 $\mu g\ L^{-1}$ in 1977 and 68 $\mu g\ L^{-1}$ in 1978 (Table 7-8), but as frequency of additions was more variable during the period of fertilization in 1977, concentrations were also more variable in that year (Fig. 7-22).

Fertilization contributed >97% of the P supplied to Mountaintop and Labelle Lakes during the periods of fertilization (Table 7-9). Very small fractions, between 0.9 and 3.5% in Mountaintop Lake and 0.9 to 1.4% in Labelle Lake, were lost via the outlet. From 14 to 25% of the P not lost to the outlet remained in the water column. The remainder, approximately 86, 78 and 75% in Mountaintop Lake in 1976, 1977 and 1978, respectively, and 72 and 84% in Labelle Lake in 1977 and 1978, respectively, was lost to the sediments (Table 7-9). The percentages were quite similar in each lake indicating that acidification of lakes does not reduce the net rate of sedimentation to, and the retention of P within lake sediments in the summer, even if supply rates of P are very high.

Prior to fertilization, TIN and TN levels were 60 and 230 $\mu g\ L^{-1}$, respectively, in Mountaintop Lake and 44 and 275 $\mu g\ L^{-1}$, respectively, in Labelle Lake. Ratios of TN:TP were 35:1 in Mountaintop Lake and 25:1 in Labelle Lake indicating that phosphorus was the element present in shortest supply (Schindler 1977).

Estimates of N budgets were cruder than P budgets because

Table 7-9. Input parameters required for calculation of phosphorus budgets in Mountaintop and Labelle Lakes. All values in kg calculated over the periods of fertilization taken to be July to October of 1976 and June to August of 1977 and 1978. Symbols as in Chapter 7B.

		J_{Exp}	J_P	J_R	L_O	ΔM	S
Mountaintop	1976	107	1.08	0.11-1.40	1.0	14.5	92.7-94.0
	1977	66.6	1.11	0.025-0.32	0.24	14.7	52.8-53.1
	1978	77.3	0.62	0.064-0.80	2.7	17.1	58.2-58.9
Labelle	1977	76.7	1.61	0.05-0.57	0.72	21.6	56.0-56.6
	1978	92.7	0.89	0.12-1.45	1.31	13.6	78.8-80.1

gaseous inputs or losses of N were not measured. Inputs of N by nitrogen fixation are quantitatively unimportant in fertilized Precambrian Shield lakes unless nitrogen-fixing blue-green algae are present (Flett et al. 1980). On only one occasion in 3 years was blue-green biomass significant in Mountaintop Lake (to be discussed), hence most of the load of N to Mountaintop Lake, at least, was most likely attributable to fertilization (Table 7-10). In 1976, TIN levels in Mountaintop Lake were much higher than in later years (Fig. 7-21), because the supply of N was highest and losses, at least in part to the sediments, were lowest in that year (Table 7-10). Maximum TIN levels of 2300 µg L^{-1} were observed in October of 1976, divided roughly equally between NH_4^+ and NO_3^-. Levels of org-N increased each year in both lakes, as did ratios of organic to total nitrogen (Table 7-8). Ratios of TN/TP were 1.7 to 3.6 times higher in Mountaintop Lake and 2.7 to 3.0 times higher in Labelle Lake (Table 7-8) than the ratios of N:P supplied (Table 7-1). This indicated that rates of loss of P (mainly through sedimentation) were greater than rates of loss of N, suggesting that N was present in excess of P in both lakes in terms of the demands of the biota, after as well as before fertilization.

iv. Major Ions and pH

Fertilization did not affect the levels of Ca^{2+}, Mg^{2+}, Na^+, K^+ or Cl^- in Labelle and Mountaintop Lakes (Appendix 6). Sulphate was the dominant anion in both lakes. Pre-fertilization SO_4^{2-} levels were 292 µeq L^{-1} in Mountaintop Lake and 327 µeq L^{-1} in Labelle Lake. Average values decreased slightly after fertilization (Appendix 6) to 280 µeq L^{-1} in 1978 in Labelle Lake and to 275 and 242 µeq L^{-1} in 1977 and 1978, respectively, in Mountaintop Lake.

Table 7-10. Input parameters for calculation of nitrogen budgets for Mountaintop and Labelle Lakes. All values in kg calculated over the periods of fertilization taken to be July to October of 1976 and June to August of 1977 and 1978. Symbols as in Chapter 7B.

		J_{Exp}	J_P	J_R	L_0	ΔM	S
Mountaintop	1976	867	23.4	10-31	70	586	244-265
	1977	369	22.0	0.9-2.9	11	104	277-279
	1978	631	13.5	0.9-2.9	11	196	438-440
Labelle	1977	509	32.0	1.7-5.2	31	260	252-255
	1978	602	20.0	1.7-5.2	27	275	321-325

The average pH (-log arithmetic mean of H+) of composite samples from Mountaintop Lake was 4.62 (4.5 - 4.8) prior to fertilization in the spring of 1976. The pH was similar to these levels (4.6 - 5.0) in May and early June of 1977 and 1978 (Fig. 7-23). Average pH values during post-fertilization periods were 4.40, 4.49 and 4.96 in 1976, 1977 and 1978, respectively. Maximum pH's observed in composite samples were 4.7, 5.1 and 5.9, respectively (Fig. 7-23). Fertilization clearly increased the pH of the Mountaintop Lake composite samples.

Vertical profiles of pH, available from 1977 to 1979 in Mountaintop Lake, indicated that the within-year decline in composite pH after June, 1977 (and most likely 1976) (Fig. 7-23) was attributable to a decline in epilimnetic pH (Fig. 7-24). Although composite pH was >5.0 in early September of 1977 and from late July to early October 1978 (Fig. 7-23), the epilimnetic pH remained <4.5 during these periods (Fig. 7-24). The pH of composite samples was high only when profundal water pH was high.

Measured pH of composite samples was always greater than the pH calculated from vertical profiles of pH corrected for morphometry. On September 27, 1978, for example, when a composite sample pH of 5.9 was recorded, samples taken at 0.5, 2, 4, 6 and 8 m had pH levels of 4.5, 4.4, 4.4, 6.3 and 6.3, respectively. Assuming no loss of H^+, the composited sample pH should have been 4.53, not 5.9. Only three profiles of DIC were measured in Mountaintop Lake. These were taken in 1979 and indicated that when the bottom waters were anoxic, hypolimnetic DIC levels were very high (Fig. 7-25) as were hypolymnetic alkalinities (Fig. 7-26). The composite samples did not, therefore, accurately reflect the pH of the lake at times of hypolimnetic anoxia, as at those times, bicarbonate from the deeper waters neutralized the epilimnetic water in the composite sample.

In Labelle Lake, the average pH of composite samples was 5.95, prior to the addition of nutrients in 1977. Fertilization changed average pH very little. It was 6.26 (6.0 -6.7) in the post-fertilization portion of 1977 and 1978. Euphotic zone pH levels rose to >8.0 during the summer (Fig. 7-27) probably because of increased algal photosynthetic activity (Schindler _et_ _al_. 1973). Hypolimnetic pH also rose over the summer in Labelle Lake, but to a much smaller extent than it did in Mountaintop Lake.

In central Ontario lakes the pH may be depressed in the spring because of the input of acidic melt-water (Jeffries _et_ _al_. 1979). The pH normally rises somewhat thereafter because of algal productivity. The decline from the already exceptionally low spring values in Mountaintop Lake is, therefore, unusual. The pH of the epilimnion declined from pre-fertilization levels of 4.5 in mid-June of 1977 to 4.0 in late July, and from 4.6 in early June of 1978 to 4.2 in mid-July (Fig. 7-24). Epilimnetic pH was not measured in 1976, but the pH of composite samples declined to a minimum of 4.3 in the summer from spring values of 4.7 (Fig. 7-23). In all three years pH increased in the late summer and fall. The decline in pH in midsummer was not attributable to direct input of acid from the atmosphere. In 1977, for example, epilimnetic pH fell from 4.5 to 4.0 between mid-June and the end of July, an increase of 68 μeq L^{-1} of H^+. The total supply of H^+ in bulk deposition was 13.4 meq m^{-2} in June and July (Chapter 2). This areal load, when increased by 20% to allow for evaporative concentration should have increased epilimnetic H^+ levels by 5μeq L^{-1} when distributed through the epilimnion (Z_{epi} = 3m). This represents only 7% of the measured increase in H^+ levels. Similar calculations indicated that precipitation supplied 5% of the acid required to depress the lake pH from 4.6 to 4.2 in 1978, and 13% of that required to depress the pH from 4.7 to 4.3 in 1976.

Another possible source of acidity is preferential utilization of NH_4^+ over NO_3^- by the phytoplankton. It is generally believed that algae take up NH_4^+ preferentially over NO_3^- (Lui and Roels 1972, McArthy et al. 1977), resulting in depressions in pH (Pratt and Fong 1940) or alkalinity (Brewer and Goldman 1976) in algal media. Assuming C:N:P ratios of 106:16:1 for algal material, ratios which must be considered to be approximate (Healey 1973), H^+ generation or consumption from NH_4^+ and NO_3^- uptake, respectively, are as follows (after Richards 1965):

$$16\ NH_4^+ + 106\ H_2O + 106\ CO_2 \rightarrow (CH_2O)_{106}\ (NH_3)_{16} + 106\ O_2 + 16\ H^+ \qquad (7\text{-}3)$$

$$16\ NO_3^- + 138\ H_2O + 106\ CO_2 \rightarrow (CH_2O)_{106}\ (NH_3)_{16} + 138\ O_2 + 16\ OH^- \qquad (7\text{-}4)$$

Assuming complete dissolution of added fertilizer in the epilimnion and no losses of NH_4^+ or NO_3^- prior to fixation in organic matter the difference between predicted and observed NH_4^+ and predicted and observed NO_3^- levels provide estimates of biotic production of acid and base, respectively. The difference between the differences, i.e. (Pred. NH_4^+ - Obs. NH_4^+) - (Pred. NO_3^- - Obs. NO_3^-), provides an overall estimate of acid generation attributable to nitrogen biochemistry. Seasonal changes in this parameter in Mountaintop Lake are plotted in Fig. 7-28.

Ammonium was utilized preferentially by the biota near the beginning of each fertilization period in Mountaintop Lake, resulting in acid generation (Fig. 7-28). Preferential utilization of NH_4^+ continued all year in 1977, the year when epilimnetic pH declined to the lowest levels observed. Differential uptake of NH_4^+ over NO_3^- could have produced 20 μeq L^{-1} of H^+ at most in 1977. While this was much more acid than contributed by bulk deposition, it was only 30% of the observed increase of 68 μeq L^{-1}. Similarly,preferential uptake of NH_4^+ could explain 17% and 60% of the observed increases in H^+ concentration during the midsummer in 1976 and 1978, respectively. Additional sources of acid were, therefore, required to explain the midsummer decline in pH. Input of acid from the watershed and input of gaseous SO_2 are two possible additional sources.

In 1976 and 1978 the pH of composite (Fig. 7-23) and epilimnetic (Fig. 7-24) samples, respectively, increased from the summer to the fall in Mountaintop Lake. Preferential utilization of NO_3^- (Fig. 7-28) provided sufficient base to explain these increases.

While the pH of the epilimnion initially decreased during fertilization of Mountaintop Lake, the pH of the hypolimnion increased (Fig. 7-24), but only during periods of anoxia (Fig. 7-18). Although data are more limited, hypolimnetic alkalinities (Fig. 7-26) and DIC levels (Fig 7-25) were also elevated during anoxic periods. Nitrate reducers (denitrifying bacteria) and/or the combined action of SO_4^{2-} and iron reducing bacteria could explain these increases in hypolimnetic pH.

Denitrification occurs only under anoxic conditions, and rates of reaction are enhanced by increasing amounts of organic matter:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 7H_2O \qquad (7\text{-}5)$$

Separate analysis of NO_3^- were not available for hypolimnetic samples. Concentrations of NO_3^--N in composite samples were 200 - 300 μg L^{-1} during spring overturn in 1977 (Fig. 7-29). Even though overturn was incomplete, this suggests that substrate for denitrifying bacteria were available in the lake. Composite levels of NO_3^--N fell to below detection limits on May 31, 1978, prior to first additions of nutrients (Fig. 7-29). As the lake was strongly stratified by the end of May in this year (surface temperature = 22°C) nutrient additions were probably restricted to the epilimnion; hence, denitrification was probably not an important contributor to hypolimnetic alkalinity in 1978.

Sulphate and iron reducing bacteria, like denitrifying bacteria are ubiquitous in the environment. They are obligately anaerobic and stimulated by organic enrichment, assuming that SO_4^{2-} and reduceable iron, respectively, are abundant.

$$2\ CH_2O + 2H^+ + SO_4^{2-} \rightarrow 2CO_2 + H_2S + 2\ H_2O \qquad (7\text{-}6)$$

$$CH_2O + 4FeOOH_{(s)} + H_2O \rightarrow 4Fe^{2+} + CO_2 + 8OH^- \qquad (7\text{-}7)$$

Both SO_4^{2-} reduction and FeOOH reduction generate alkalinity, as indicated above. The alkalinity generated by equation 7-6 is lost if reduced iron reacts with the H_2S to form insoluble FeS as below.

$$Fe^{2+} + H_2S + 2OH^- \rightarrow FeS_{(s)} + 2H_2O \qquad (7\text{-}8)$$

The alkalinity generated by reduction of the iron oxide (equation 7-7), however, will be preserved by precipitation of FeS.

Schindler et al. (1980) have suggested that bicarbonate generated by sulphate reducing bacteria in Lake 223, in northwestern Ontario, consumed a large fraction of the sulphuric acid added to the lake. At different times sulphate, nitrate and ferric hydroxide reduction might also explain the increase in alkalinity and pH in the hypolimnion of Mountaintop Lake, especially as the increases occurred during times of anoxia and in the presence of large amounts of organic matter attributable to fertilization.

King et al. (1974) have suggested that rates of recovery of acidic strip-mine lakes may be enhanced by the addition of organic matter, resulting in anoxia and the stimulation of sulphate reducers. In one two month experiment in which acidic strip-mine lake water was combined with raw sewage sludge in a laboratory microcosm, they observed an increase in pH from ~3.0 to ~8.0, and decreases in SO_4^{2-} from ~1900 to ~250 mg L^{-1}. Concentrations of Fe fell from ~25 to <1 mg L^{-1} and acidity from ~420 to 0 mg L^{-1} as $CaCO_3$. Despite this apparently large capacity to consume H^+, 2 factors ensure that the stimulation of SO_4^{2-} reduction may not be useful as a "restorative" tool for acidic lakes in Ontario, or as a prophylatic tool for maintaining alkalinity in lakes of declining buffering capacity. The mechanism requires anoxia, a condition that will eliminate many fish populations, such as lake trout. It also requires organic matter, which in the case of Mountaintop Lake was produced by fertilization. The resultant decreases in transparency are clearly undesirable.

v. Phytoplankton

a. Phytoplankton Productivity and Biomass

Rates of carbon uptake in Mountaintop Lake were measured on only five occasions, one of which preceded fertilization in 1976.

Incubations were started at sunrise to minimize chances of carbon depletion (Schindler and Fee 1973). Maximum hourly volumetric production rates were many times higher after fertilization than the production rate measured before fertilization (Table 7-11). Assuming no carbon limitation, daily production rates were also increased by fertilization. Estimates of daily productivity were, however, undoubtedly overestimates, as uptake rates calculated assuming no carbon limitation would have resulted in depletion of the DIC available in the early morning by 24, 93, 26 and 19% on July 14, 27, August 10 and August 24, respectively. Such high rates of depletion strongly suggest that algal photosynthesis would have been limited by carbon availability during the day (Schindler and Fee 1973)

Schindler (1977) has demonstrated that lack of carbon does not prevent the eutrophication of Precambrian Shield lakes. In Mountaintop Lake, neither the diel carbon limitation nor the low euphotic zone pH prevented the development of very large standing stocks of phytoplankton. In the post-fertilization portion of the ice-free season, average phytoplankton biomass increased from 0.96 to 2.65 to 7.17 mg L^{-1} and average chlorophyll a from 5.7 to 20.1 to 64.8 mg m^{-3} in 1976, 1977 and 1978, respectively. Levels of chlorophyll a exceeded 100 mg m^{-3} in the late summer of 1978 (Fig. 7-30). The maximum phytoplankton biomass of ~14 mg L^{-1}, observed in 1978 (Fig. 7-31), is as high as the maximum biomasses observed in the western basin of Lake Erie (Vollenweider et al. 1974), despite a euphotic zone pH of 4.0 to 4.5. It is also as high or higher than the maximum biomass observed by Findlay (1978) in Lakes 226 North, 304 and 261, all non-acidic Precambrian Shield lakes in northwestern Ontario that were fertilized with P or N and P. On a plot of

Table 7-11. DIC concentrations and several measures of productivity in Mountaintop Lake on one day prior to fertilization (June 29) and on four days during fertilization in 1976. Data are not corrected for morphometry. Daily estimates are calculated assuming no DIC limitation and are most likely overestimates (see text). Number in parentheses is depth (m) of maximum productivity.

	Carbon Uptake (mg)				DIC
Date	$m^{-3}_{max}hr^{-1}$	$m^{-3}hr^{-1}$	$m^{-3}day^{-1}$	$m^{-2}day$	(mgm^{-3})
June 29	0.9(4.5)	0.51	6.2	56	350
July 14	3.4(0.3)	1.2	35.3	326	150
July 27	13.1(0.75)	5.6	93./3	652	100
Aug. 10	7.4(0.1)	2.7	18.9	152	350
Aug. 24	8.6(0.1)	2.3	18.9	153	100

ice-free period average phytoplankton biomass vs. TP, data from Mountaintop and Labelle Lakes could not be separated (Fig. 7-32). It is clear, in summary, that acidification of lakes will not prevent the development of symptoms of eutrophication that might accompany increases in rates of nutrient supply. This strongly supports the suggestion of Schindler (1980) that "oligotrophication" of lakes will not be a consequence of their acidification.

While maximum biomass of phytoplankton in Mountaintop and Labelle Lakes was as great as that observed in several fertilized lakes in northwestern Ontario, the slope of the TP-biomass regression equation for data averaged over the ice-free period was generally much lower than for ELA Lakes (Schindler _et_ _al_. 1978 and Fig. 7-32). This is surprising as rates of nutrient supply were greater for Mountaintop and Labelle Lakes than for ELA lakes. The greatest rate of supply of P to an ELA Lake (Lake 227), for example, was ~600 mg m^{-2} yr^{-1} of P (Schindler _et_ _al_. 1978), or 4mg m^{-2} day^{-1} over a 21 week fertilization period, assuming a natural P input of 50 mg m^{-2} yr^{-1} evenly distributed over the year. Supply rates of P to Mountaintop and Labelle Lakes were 4 to 5 times this amount (Table 7-1).

One possible explanation for the reduced response to fertilization is that frequency and total duration of additions are very important in determining long-term response. Schindler _et_ _al_. (1978) noted that ELA lakes were fertilized continuously (1975) or in 20 or 21 equal weekly additions beginning in mid-May. In contrast, Mountaintop and Labelle Lakes were fertilized with P once every 9 - 13 days on average for between only 10 and 15 weeks.

In Mountaintop and Labelle Lakes the ratio of phytoplankton biomass to TP or to J (the total volumetric supply of P) was inversely correlated with zooplankton biomass. This suggests that grazing activities of the zooplankton may have exerted some control over phytoplankton standing stocks (to be discussed). A comparison of the response of the phytoplankton of Mountaintop and Labelle Lakes to fertilization should, therefore be restricted to years with similar zooplankton biomass, i.e. to both years in Labelle Lake and to 1977 only in Mountaintop Lake (Table 7-12). In these three years the yield of phytoplankton biomass per unit rate of supply of P was very similar (1060 - 1330 mg of plankton mg^{-1} of P day^{-1}). This comparison also indicates that acidification of Mountaintop Lake did not limit phytoplankton yield.

b. Community Structure

Prior to fertilization, the unproductive nature of Mountaintop Lake was indicated by low chlor a levels (0.4 - 0.9 mg m^{-3}). Phytoplankton biomass varied from 0.05 to 0.67 mg L^{-1} prior to fertilization (Fig. 7-31). *Rhizosolenia longiseta* Zach. was the common dominant in mid-June, followed by chrysophytes, especially *Dinobryon bavaricum* Imhof, *D. sertularia* var. *protruberans* (Lemm.) Krieger and *Mallomonas crassiquama* (Asmund) Fott in late June (Fig. 7-33).

Fertilization began on July 8, 1976 when phytoplankton biomass was very low (0.05 mg L^{-1}). The major response to fertilization was an increase in cryptomonads, especially an unidentified species of *Cryptomonas* (Fig. 7-33), which had a maximum biomass of 5.28 mg L^{-1} on August 5 (Fig. 7-31). Total phytoplankton biomass fell to very low levels in September, 1976, despite continued fertilization. The decrease in biomass was associated with very dense populations of herbivorus zooplankton (to be discussed).

Dominant phytoplankton species prior to fertilization in the

Table 7-12. Ice-free period average rate of supply of P (J), concentration of TP, phytoplankton and zooplankton biomass in Mountaintop and Labelle Lakes. Ratios of phytoplankton biomass to TP and J are included.

		TP ($mg\ m^{-3}$)	J^1 ($mg\ m^{-3}\ day^{-1}$)	$Phyto^2$ ($mg\ m^{-3}$)	Zoo^2 ($mg\ m^{-3}$)	$\frac{Phyto}{TP}$	$\frac{Phyto}{J}$
Mountaintop	1976	39	1.89	700	128	18	370
	1977	54	1.50	2000	49	37	1330
	1978	78	1.74	6900	2	88	3970
Labelle	1977	46	1.51	1600	31	35	1060
	1978	64	1.83	2400	72	38	1310

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[1] calculated over May to November inclusive assuming only additions were fertilization. See Table 7-9.

[2] Phyto and Zoo are wet and dry weights, respectively.

spring of 1977 were the small colonial blue-green Synechococcus sp., which was replaced in early June by an unidentified dinoflagellate and the chrysophytes Mallomonas sp., Dinobryon bavaricum, D. divergens Imhof and D. sertularia Ehr.. Biomass increased more rapidly than in 1976 after the onset of fertilization. Cryptomonas sp. was again dominant, although species of Closterium, Chlamydomonas, Mallomonas and Gymnodinium all formed 5-10% of the biomass for short periods of time (Fig. 7-31, 7-32).

In 1978 fertilization raised concentrations of TP more rapidly than in 1976 or 1977 (Fig. 7-21), and phytoplankton biomass was greater and community structure different than in the two previous years. In early June, dinoflagellates were dominant as Peridinium inconspicuum Lemm. attained a peak biomass of 2.8 mg L^{-1}. Other dominant species in June and early July were Cryptomonas sp. (maximum biomass 2.3 mg L^{-1}), Chlamydomonas sp. (maximum biomass 6.1 mg L^{-1}) and Oscillatoria sp. (maximum biomass 3.0 mg L^{-1}). From mid-July to November, only four taxa made contributions of >1% to phytoplankton biomass, namely Chlamydomonas sp., Cryptomonas sp., Oscillatoria sp. and Dictyosphaerium pulchellum Wood. Of these, D. pulchellum was dominant, forming 92% of the biomass from August to November (Fig. 7-32), and attaining maximum levels of 13.3 and 14.5 mg L^{-1} on July 26 and Oct. 4, respectively (Fig. 7-31).

The phytoplankton community structure, resulting from fertilization, in Labelle Lake was quite different from that in Mountaintop Lake. Fertilization in Labelle Lake began on June 15, 1977 and was quickly followed by a bloom of Cyclotella sp. (biomass 3.25 mg L^{-1}) which formed 89% of the total biomass one week after the first addition of nutrients. For most of July and August, however, green algae were dominant. Species of *Scenedesmus*, especially *S. abundans* (Kirchner) Chod. and *S. ecornis* (Ralfs) Chodat were most important. In the latter half of August and September, blue-greens, especially *Oscillatoria limnetica* Lemm. and *O. geminata* (Meneg.) Gomont shared dominance with *Scendesmus* (Fig. 7-34 and 7-35).

The highest biomass observed in Labelle Lake occurred on June 13 of 1978, within two weeks of the onset of fertilization. Biomasses of 9.0 mg L^{-1} for *Scenedesmus* sp., mainly *S. intermedius* var. *bicaudatus* Hortob and *S. acutus* Meyen, and 1.1 mg L^{-1} for *Synedra ulna* (Nitz.) Ehr. were mainly responsible for this maximum. Blue-greens, mainly *Oscillatoria Lauterborni* Schmidle replaced *Scenedesmus* as dominants in early July and peaked in biomass at 3.1 mg L^{-1}. *O. Lauterbornii* was replaced as a dominant by *S. ecornis* after late July of 1978 (Fig. 7-34). Other green genera, especially *Chlamydomonas*, *Micractinium*, *Dictyosphaerium*, *Monoraphidium* and *Ankistrodesmus*, were quite common in Labelle Lake in 1978. Except for *Kirchneriella lunaris* (Kirch.) Moebius and *K. subsolitaria* G.S. West, which had a joint biomass of 1.0 mg L^{-1} on Oct. 17, the biomass of these other genera never exceeded 1.0 mg L^{-1}.

Langford (1950) reported that fertilization of Shield lakes in Algonquin Park, Ontario, resulted in increases in phytoplankton standing stocks, especially that of diatoms. While diatoms certainly may be the dominant algae in eutrophic lakes (Nicholls 1976), additions of nitrogen and phosphorus to Precambrian Shield lakes have more commonly resulted in increases in the standing stocks of green and/or blue-green algae (Smith 1969, Schindler *et al*. 1971, Schindler *et al*. 1973, Findlay 1978), as in Labelle Lake.

Patterns of community dominance typically change over the course of the ice-free season in fertilized lakes. Fertilized with N and P as was Labelle Lake, the phytoplankton dominants of Lake 227, in northwestern Ontario, changed over the ice-free season from cryptomonads to greens in 1974, from cryptomonads to greens to blue-greens to chrysophytes in 1975 and from blue-greens to greens in 1976 (Findlay 1978). Dominance in Labelle Lake changed from diatoms to greens to blue-greens in 1977 and from greens to blue-greens and back to greens in 1978.

Mountaintop Lake differed from this more typical pattern both in the persistance and in the identity of the community dominants. The dominance of cryptomonads in 1976 and 1977 is perhaps not surprising given their tolerance of environments of high acidity (Chapter 1). Once established, the low diversity of the phytoplankton community of Mountaintop Lake, a characteristic of acidic lakes, perhaps facilitated the persistence of cryptomonads as dominants until the end of 1977. Why _D. pulchellum_ emerged as dominant in 1978, replacing several other taxa, is unclear.

vi. Planktonic Crustacea and Rotatoria

Species richness of planktonic crustacea in Mountaintop Lake was only about 50% of that observed in Labelle Lake. This reduction is typically observed in acidic lakes (Chapter 1). The richness of the rotifer community was less reduced in comparison with Labelle Lake than that of the crustacean community (Table 7-13).

Eleven species of crustacean zooplankton were identified in Mountaintop Lake collections (see Appendix 8). The common species of Cladocera were _Bosmina longirostris_ O.F. Muller and _Chydorus sphaericus_ O.F. Muller, which occurred in 84 and 59% of the samples, respectively. Excluding immature stages, _Diaptomus minutus_ Lilljeborg and _Cyclops vernalis_ Fischer were the common copepods,

Table 7-13. Summary of rotifer[1] and crustacean zooplankton data from Mountaintop and Labelle Lakes. All values are ice-free period averages.

Lake	Year	Number of Species per collection		Biomass	% Biomass		
		Rotatoria	Crustacea	(mgm^{-3})	Rotatoria	Cladocera	Copepoda
Mountaintop	1976	5.6	3.6	160	9	39	52
	1977	5.8	4.1	94.8	49	2	49
	1978	5.5	3.5	3.8	46	2	52
Labelle	1977	6.5	7.1	35.5	13	3	84
	1978	7.0	6.8	78.6	8	4	88

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[1] Rotifer densities converted to biomasses using dry weights provided by Lawrence et al. (in press), except for the weight of Keratella taurocephala which was determined from Clearwater Lake collections

occurring in 94 and 41% of the samples, respectively. These are the common dominant species in Sudbury-area acidified lakes (Chapter 1). Fifteen crustacean species occurred in Labelle Lake. B. longirostris and Diaphanosoma leuchtenbergianum* Fischer were the most common cladocerans. They were identified in 100 and 91% of the samples, respectively. The common copepods were Diaptomus oregonensis Lilljeborg, Tropocyclops prasinus mexicanus Kiefer, D. minutus, Mesocyclops edax Forbes, Cyclops scutifer Sars and Epischura lacustris Forbes, which were observed in 100, 91, 77, 77, 68 and 41% of the collections, respectively.

Eighteen species of rotifers were identified in Mountaintop Lake (Appendix 8). Those forming more than 10% of the ice-free period average density of rotifers were Keratella cochlearis (Gosse) in 1978 only, and K. taurocephala Myers and a species of Synchaeta in all years. In Labelle Lake, 16 species of rotifers were identified. Keratella quadrata (Muller), K. taurocephala, Kellicottia bostoniensis (Rousselet), Kellicottia longispina (Kellicott) and Polyarthra vulgaris Carlin formed between 1 and 5% of the total abundance in 1977 and/or 1978. By far the most important species, however, was K. cochlearis, which formed 85% of the total rotifer density in 1977 and 88% in 1978.

In 1976 crustaceans contributed far more to total biomass in Mountaintop Lake than did rotifers. Together, D. minutus and B. longirostris accounted for 97% of the crustacean biomass in this year. D. minutus copepodids were dominant prior to fertilization in 1976, but B. longirostris gradually replaced D. minutus as the dominant species after fertilization (Fig. 7-36). Maximum densities of B. longirostris (424 L^{-1}) and D. minutus (60 L^{-1}) occurred in early October. Together they formed the highest biomass (437 mg m^{-3}) observed in the lake. Very high densities of B. longirostris have previously been observed by Haney (1973) in an acidic, brown water lake.

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*Some specimens could not be distinguished from D. brachyurum

These very high densities of herbivorous zooplankton were probably responsible for the large contemporaneous decline in phytoplankton biomass (Fig. 7-31). Haney (1973), using radiotracer techniques, measured filtering rates of 0.45 mL $animal^{-1}$ day^{-1} for B. longirostris and 2.1 mL $animal^{-1}$ day^{-1} for D. oregonensis in acidic Drowned Bog Lake. Applying these rates to B. longirostris and D. minutus in Mountaintop Lake suggests that at their maximum densities, the zooplankton of Mountaintop Lake may have filtered 32% of the lake volume per day clear of prey. This estimate may in fact be a substantial underestimate for Bosmina (Haney and Hall 1975). Morgan and Kalff (1979) indicated that under ideal laboratory conditions maximum division rates for Cryptomonas, the dominant phytoplankter in Mountaintop Lake, are about 1 division day^{-1}. Because of self-shading and diel carbon limitation, division rates in Mountaintop Lake would probably have been much less than the rate under optimal conditions. It appears, therefore, that grazing rates of the zooplankton at the time of maximum zooplankton density were sufficiently high to reduce phytoplankton biomasses.

While fertilization resulted in an increase in zooplankton biomass in Mountaintop Lake in 1976, the year to year trend after fertilization in Mountaintop Lake was a reduction in crustacean biomass with each year of fertilization (Table 7-13). Average crustacean densities also decreased from 84 animals L^{-1} in 1976 to

50 in 1977 and to 3.6 animals L^{-1} in 1978.

In 1977, densities were as high at the beginning of the year as they had been prior to fertilization. D. minutus was the most important species. Typically, abundances of adult D. minutus are at a maximum in the late summer and fall (Schindler and Noven 1971, Davis 1972) in Shield lakes or in the winter in Lake Ontario (Czaika 1974). The species is very tolerant of acidic environments and has been shown to increase in densities after fertilization of a Shield lake (Smith 1969). Despite this, densities of D. minutus fell to very low levels in August of 1977 and did not recover in the remainder of 1977 or in 1978 (Fig. 7-36). In fact, biomass of all zooplankton was very low in 1978 (Fig. 7-36).

Coincident with the latter stages of the decrease in D. minutus densities in 1977 was a tremendous increase in rotifer densities (Fig. 7-37). The dominant rotifers were K. taurocephala with a maximum density of 5400 animals L^{-1} and biomass of 109 mg m^{-3} on Aug. 31, and Synchaeta sp. with maximum abundance of 344 animals L^{-1} and biomass of 89.5 mg m^{-3} on the same date. Rotifers so outnumbered crustacean zooplankton at this time (~500:1) that samples resembled pure cultures of rotifers with the odd crustacean contaminant.

There is some evidence (Pouriot 1963, in Hutchinson 1967) that Keratella can feed on cryptomonads; hence, they could have competed with D. minutus for the available dominant phytoplankter. As peak abundances of rotifers occurred after the decline in D. minutus, it would not appear that competition with rotifers resulted in the decline in numbers of D. minutus. Despite their very high densities, rotifers did not substantially deplete phytoplankton populations as had the crustacean community at its maximum density in the previous year.

Unlike Mountaintop Lake, ice-free period average densities of crustacean zooplankton increased from 31 animals L^{-1} in Labelle Lake in 1977 to 55 animals L^{-1} in 1978. Biomasses of crustacea increased from 31 to 72 mg m^{-3}. A comparison of data collected prior to Sept. 12 (which corrects for differences in sampling duration in the two years,Fig. 7-38) also indicated that biomass and densities approximately doubled from 1977 to 1978.

Cladocera formed <4% of the average biomass in each year in Labelle Lake, although their biomass did increase in August and September of 1978 (Fig. 7-38). Peak densities of cyclopoid copepods were observed in June and July of 1977 and in May, June and September of 1978 (Fig. 7-38). The spring maximum in each year was comprised mainly of _C_. _scutifer_, _T._ _prasinus_ _mexicanus_ and _M_. _edax_ in 1977 and by _C_. _scutifer_ and _T_._p_. _mexicanus_ in 1978. The 1978 September maximum was attributable to _T_. _prasinus_ _mexicanus_ and _M_. _edax_.

The most important contributors to total biomass in both years in Labelle Lake were calanoid copepods (Fig. 7-38). _E_. _lacustris_ occurred in June of both years, but numbers never exceeded 0.15 animals L^{-1}. _D_. _minutus_ and _D_. _oregonensis_ were the only other calanoids observed, and fertilization was accompanied by a replacement of _D_. _minutus_ by _D_. _oregonensis_ (Fig. 7-39). Adult _D_. _oregonensis_ formed 3% of the density and 10% of the average biomass in 1977. They formed 21% of the density and 57% of the biomass in 1978, and at their peak in November 1978, adult _D_. _oregonensis_ contributed 92% of the maximum crustacean biomass of 136 mg m^{-3} observed in Labelle Lake (Fig. 7-38). _D_. _oregonensis_ and _D_. _minutus_ sympatrically occur in a large number of Ontario Shield lakes (Rigler and Langford 1967, Carter _et_ _al_. 1980).

However, Patalas (1971) found that in Shield lakes in northwestern Ontario, D. oregonensis was observed more frequently in shallow, small, coloured lakes than D. minutus. D. oregonensis is the only calanoid copepod found in many eutrophic lakes in Ontario (Hitchin 1976, Strus 1976); hence, its replacement of D. minutus after the fertilization of Labelle Lake was not surprising.

Rotifer densities reached a maximum in September in both years in Labelle Lake (Fig. 7-40). They outnumbered crustacean zooplankton by about 10:1 on average, but formed only 13% and 8% of the biomass in 1977 and 1978, respectively (Table 7-13). This fraction does, however, represent a substantial increase in rotifer importance over levels typically observed in Shield lakes (<3%, Chapter 1). K. cochlearis was the most important species.

A range of differential responses of rotifers and crustaceans to nutrient additions have been observed. At one extreme, Langford (1950) noted that most of the increase in zooplankton densities observed in fertilized lakes in Algonquin Park was attributable to rotifers. After fertilization of Great Central Lake in British Columbia, Lebrasseur and Kennedy (1972) observed equal increases in rotifer and crustacean components of the zooplankton. At the other extreme, Smith (1969) suggested that while responses of rotifers in fertilized Crecy Lake in New Brunswick were not predictable, populations of D. minutus, the dominant crustacean, always increased after fertilization. Given this diversity of responses, the observation that rotifers increased proportionally more in Mountaintop Lake than in Labelle Lake cannot be unequivocably ascribed to the acidity of Mountaintop Lake.

The most important difference in the response of the zooplankton communities of Mountaintop and Labelle Lakes to fertilization was a trophodynamic response. In the non-acidic lake (Labelle Lake) increases in phosphorus concentrations were reflected up the food chain in increases in both phytoplankton and zooplankton. Powell (personal communication) has also noted a very healthy inshore fish community dominated by fathead minnows in Labelle Lake. In Mountaintop Lake, in contrast, increases in phytoplankton biomass stimulated by fertilization, resulted, ultimately in a reduction in zooplankton biomass to levels well below those observed prior to fertilization and well below those typically observed in acidic lakes.

The decline of D. minutus densities in August of 1977 in Mountaintop Lake was not attributable to physical or chemical stresses. It occurred at a time when vertical variations in pH (4.2 at the surface to 5.0, 1 m above bottom) were not extreme for the lake, and when only the bottom 1 m was anoxic (Fig. 7-18). There was no large contemporaneous change in phytoplankton biomass (Fig. 7-31), and as Cryptomonas was dominant both before and after the crash in herbivore densities, at biomasses greater than in 1976 when no crash occurred, it must be assumed that the food base for D. minutus was adequate. Concentrations of the potential toxins Cu and Ni, attributable to smelter activities in Sudbury, were not greater after fertilization in 1977 than in 1976 (Table 7-7). Because of the low pH virtually all added NH_4^+ was ionized and therefore not toxic. Densities of predacious cyclopoid copepods remained very low prior to and during the crash. Chaoborus larvae were present in the lake, however, and their predation probably caused the mid-summer zooplankton collapse in 1977, and restricted populations to low densities in 1978.

vii. *Chaoborus*

a. *Life History*

Chaoborus flavicans was the only species of *Chaoborus* identified in Labelle Lake. It was observed on only two occasions and had a maximum density, represented by only two captured animals, of approximately 0.02 animals L^{-1}. Roth (1968) and Stahl (1966) have reported that *C. flavicans* usually resides in the deeper waters or surficial sediments during the day. Because sampling for *Chaoborus* was exclusively diurnal in Labelle Lake, densities may have been underestimated. However, as Labelle Lake supports a substantial fishery dominated by a known *Chaoborus* predator, the fathead minnow (Lynch 1979), *Chaoborus* populations were probably not large in the lake.

Larvae of *Chaoborus albatus*, *Chaoborus flavicans* and *Chaoborus americanus* were identified in Mountaintop Lake collections. *C. albatus* occurred sporadically in 1977 at very low densities. *C. flavicans* and *C. americanus* were equally abundant in 1976, but in 1977 and 1978, third and fourth instars of *C. americanus* (and presumably the other instars) accounted for 90% of the animals encountered. In the subsequent discussion the reported magnitude of *C. americanus* includes this small contribution of *C. flavicans.*

C. americanus is a more frequent inhabitant of fishless lakes in eastern Canada than in lakes with a resident fishery (Pope *et al*. 1973, Carter *et al*. 1980). In fishless Mountaintop Lake, average summer densities (June to mid-September) increased each year, from 31 to 591 to 1083 animals m^{-3} in 1976, 1977 and 1978, respectively. The maximum density observed was 10,700 animals m^{-2} (2500 m^{-3}) on June 20, 1978. This is an order of magnitude higher than the maximum areal density of all species of Chaoborus reported by Pope et al. (1973) from any of 26 lakes in the Matamek River watershed in Quebec.

While larvae of most Chaoborus species may be planktonic only at night, C. americanus is often planktonic at all times, especially in fishless lakes (Fedorenko and Swift 1972, Carter and Kwik 1972). This suggests that the diurnal samples of C. americanus in Mountaintop Lake provided an accurate estimate of population densities.

Carter and Kwik (1977) reported that C. americanus had a two year life cycle in Lac Gallienne in Quebec. In Mountaintop Lake it had a one year life cycle (Fig. 7-41b) as in Eunice Lake in British Columbia (Fedorenko and Swift 1972). Animals overwintered as fourth instar larvae (larval instars separated by head capsule lengths, Fig. 7-42), emerging from late May to mid-July in 1977. Emergence was complete by the end of June in 1978, hence peak abundances of first instar larvae occurred earlier than they had in 1977. The T_1 occurred on July 9 in 1977 and much earlier, on June 16 in 1978 (Table 7-14). The T_k is the mean date of occurrence of instar k weighted by its abundance.

The progression from first to second instar was as rapid in 1977 as in 1978. T_2-T_1 was 9 days in both years (Table 7-14). As T_2-T_1 was less than the average duration between samples (14 days), it is possible that peak abundance of early instar larvae was, in fact, underestimated. Progression from second to third instar was much slower in 1978 (35 days) than in 1977 (10 days). Rates of progression from third to fourth instars were not comparable in 1977 and 1978 as sampling continued further into the fall of the latter year (Fig. 7-41). However, as all Chaoborus were fourth instar by mid-September of 1977 but not until the end of October in 1978, it appears that the rate of progression from third to fourth instar was also slower in 1978 than in 1977. As the size of the second, third, and especially of fourth instar animals was also reduced in 1978, it is clear that Chaoborus growth rates were much lower in 1978 than in 1977 (Table 7-14). Data from 1976 were to sparse to compare rates of progression through instars with later years.

b. Chaoborus Densities and Prey

Neill and Peacock (1980) have indicated that differences in densities of latter instar Chaoborus larvae may be attributable to differences in mortality rates of early instar larvae, which in turn are correlated with differences in prey densities. To determine if prey densities could explain the observed differences between years in densities of latter instar Chaoborus larvae we estimated the standing stock of available prey for early instar (1 and 11) larvae and compared this with minimum estimates of Chaoborus food requirements or rations. Since the preferred prey of early instar Chaborus are small zooplankters, such as rotifers and copepod nauplii (Pastorok 1980), we considered the sum of rotifer and naupliar biomasses to be an estimate of the biomass of available prey. The daily weight gain of Chaoborus larvae was used as a minimum estimate (assuming no respiratory or other losses) of their daily food requirement or ration. Assuming that growth is exponential between T_k values and initial (B_k) and final (B_{k+1}) individual biomasses are equal to the average instar weights at the T_k (Table 7-14), then a daily growth rate (r), which can serve as a minimum daily ration, can be calculated from tne following:

$$B_{k+1} = B_k e^{r(T_{k+1}-T_k)} \qquad (7\text{-}9)$$

where k represents an instar number.

The minimum daily rations or growth rates between instars calculated in this way were much lower in 1978 than in 1977 (Table 7-14), indicating that the animals grew faster in 1977. The calculated rations are, of course, minimum estimates of required daily food intakes, as most ingested food would not be reflected in larval growth. Nevertheless, daily rations calculated for growth from first to second and second to third instar larvae in 1977, 16% and 14% respectively, are higher than previously published daily food intakes of Chaoborus measured for confined animals. Pastorok (1980) noted that intakes averaged 4.6% of larval weight per day for second to fourth instar larvae. The range was 0.6 - 13.2% day^{-1}. Our higher calculated rates support the suggestion of Lewis (1979) that predatory behaviour of Chaoborus may be inhibited when animals are confined to measure predation rates.

A minimum daily ration for all first and second instar larvae in Mountaintop Lake was calculated as the product of the larval densities and the appropriate minimum daily ration for individual larvae (Table 7-15). When the sum of rotifer and naupliar biomasses (mg m^{-3}) was divided by this minimum ration (mg m^{-3} day $^{-1}$), a maximum prey inventory (days) was obtained. This provided an estimate of the instantaneous availability of prey measured as the number of days that Chaoborus predation could continue at the calculated rations before prey were exhausted (Table 7-15).

Prey inventories were not calculated for 1976 data as the number of larvae captured in samples was small and life history, in consequence, uncertain. Prey availability in July of 1977 was,

Table 7-14. Weighted mean date of occurence of instar k (T_k), average dry weights and lengths of instars and growth rates (r) between mean dates of occurrence of instars of *Chaoborus* in Mountaintop Lake in 1977 and 1978.

	Instar							
	1977				1978			
	I	II	III	IV	I	II	III	IV
T_k	July 9	July 18	July 28	Sept. 7[1]	June 16	June 25	July 30	Sept. 24[1]
length (mm)	2.5	4.6	6.5	9.7	2.7	3.6	6.3	7.6
weight[2] (µg)	4.3	17.8	68.8	622	4.7	9.0	57.8	147
r[3] (% day^{-1})		15.8	13.5	5.5[1]		6.4	5.3	2.1[1]

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[1] T_4 and r from T_3 to T_4 values are not comparable between years because of different sampling intensities in the fall.

[2] calculated by linear interpolation to the T_k from measured biomasses on two days, one before and one after the T_k. This weight was used to calculate *Chaoborus* biomass in Table 7-15.

[3] calculated as stated in text.

Table 7-15. Average monthly biomass of first and second instar Chaoborus and copepod nauplii and rotifers (preferred prey) in Mountaintop Lake. A minimum daily food requirement for Chaoborus (Ration) and a maximum prey inventory (a ratio of the sum of naupliar and rotifer biomasses to ration) are included.

Date	Biomass			Minimum Ration[2] (μg dry weight $m^{-3}day^{-1}$)	**Maximum** Prey Inventory (days)
	Chaoborus[1]	Nauplii (mg m^{-3}dry weight)	Rotifer		
June 1976	-	5.18	9.50	-	-
July 1976	-	0.92	1.75	-	-
August 1976	-	2.63	6.30	-	-
June 1977	2.01	4.52	2.75	279	26
July 1977	5.43	1.25	37.5	760	51
August 1977	1.21	1.74	74.3	164	460
June 1978	12.1	1.26	0.09	732	1.8
July 1978	2.6	4.19	3.90	141	62
August 1978	0.05	0.22	5.80	2.5	2400

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[1] 1976 data excluded as numbers of captured animals were too low to permit accurate calculation of biomass.

[2] calculated as the sum of the products of Chaoborus densities and minimum food requirements (r in % body weight day^{-1}). Values of r were 16% and 6% for 1st instar larvae, and 14% and 5% for 2nd instar larvae in 1977 and 1978, respectively. See Table 7-14.

however, much higher than in July of 1976, perhaps explaining the much higher survivorship of first and second instar larvae, resulting in larger numbers of older instar larvae in 1977. In June 1978, there were insufficient stocks of nauplii and rotifers to support the very high densities of first and second instar Chaoborus. The prey inventory was only 2 days (Table 7-15). This is many times less than the potential renewal rates of Keratella (Makarewicz and Likens 1979), the dominant rotifer included in the prey. The prey inventory inluding all crustaceans and rotifers increased to only 4 days in June 1978. This suggests that an additional food source must have been exploited by the early instar larvae to account for the high densities of latter instar larvae in 1978.

In 1978, Chaoborus larvae were diurnally planktonic (Fig. 7-43) indicating that they were probably not feeding on benthic micro-invertebrates. However, phytoplankton or planktonic protozoa could have been exploited as prey in June of 1978. Algae can serve as a food source for Chaoborus larvae when their preferred prey are scarce (Pollard 1976 in Pastorok 1980). Swuste et al. (1973), in fact, raised Chaoborus from eggs to pupae entirely on a diet of filamentous algae. The algal biomass of the lake was very high, ranging from 2 to 9 mg L^{-1} in June 1978. Assuming a wet to dry weight ratio of 4.5:1 for algae, algal biomass exceeded the sum of naupliar and rotifer biomass by between 2 and 3 orders of magnitude.

Protozoa were also very abundant in June of 1978. When preserved phytoplankton samples from that month were re-examined for protozoa (enumerated in a manner similar to phytoplankton), average protozoan biomass was calculated to be ~100 mg m^{-3} dry weight, assuming a wet to dry weight ratio of 4.5. Protozoan biomass was therefore about 2 orders of magnitude higher than the sum of rotifer and naupliar biomasses in that month. Protozoa were not identified, but the dominant forms were spherical cells with mean diameter of 16 μm and ellipsoidal cells with mean dimensions of 25 x 18 x 8 μm. At these very high biomasses both protozoa and phytoplankton could have been exploited by the early instar Chaoborus, thus reducing early instar mortality. Whatever the source of prey for the early instar larvae, reduced body size of latter instar larvae (Table 7-14) indicated that they were not thriving on a diet containing little of their preferred prey.

c. Chaoborus Predation

Pastorok (1980), in reviewing the literature on Chaoborus predation rates, reported a mean predation rate (with range in parentheses) of 5.3 (0.4 - 28) prey day^{-1} for second, third and fourth instar larvae of five species of Chaoborus, excluding C. americanus, offered numerous species of planktonic crustacea as prey. Predation rates vary more with prey density and larval size than with species of Chaoborus, hence predation rates of C. americanus fall well within this range (Fedorenko 1975, Lynch 1979).

To deduce if predation by Chaoborus in Mountaintop Lake could explain the large observed decreases in the density of D. minutus (Fig. 7-41), the dominant zooplankter in 1977, the decrease in densities of D. minutus adults and copepodids between sampling dates was expressed as an inferred predation rate (prey Chaoborus^{-1} day^{-1}). This was calculated as the rate of decrease in density of D. minutus (prey L^{-1} day^{-1}) divided by the average density of second, third and fourth instar Chaoborus. Agreement between inferred predation rates and previously reported values was considered to be strong evidence that Chaoborus predation was responsible for the observed mortality of *D. minutus*. All calculated predation rates were well within or lower than the range of *Chaoborus* predation rates reported within the literature (Table 7-16). Recalling that Lewis (1979) has indicated that reported predation rates may be underestimates, the collapse of the herbivorous zooplankton community in 1977 in Mountaintop Lake, and the failure of the community to recover in 1978 when *Chaoborus* densities were even higher than in 1977 can be attributed to *Chaoborus* predation.

In fishless, non-acidic lakes smaller herbivores are replaced by larger herbivores as *Chaoborus* predation increases (Lynch 1979). As large species of zooplankton had been eliminated during the acidification of Mountaintop Lake, their densities obviously did not increase following the reduction in densities of small crustacean herbivores. However, the densities of a herbivorous and a predacious rotifer increased substantially (Fig. 7-41a) immediately after the crash of *D. minutus* (Fig. 7-41c). Rotifers are too small to be preferred prey for third and fourth instar *Chaoborus* (Pastorok 1980).

The response of the zooplankton community of Mountaintop Lake to fertilization in the presence of (1977 and 1978) and in the virtual absence of (1976) *Chaoborus* is summarized in Fig. 7-44, a three-dimensional phase plane diagram in which temporal trajectories represent sequential changes at monthly intervals in *Chaoborus* densities, and in the biomass of phytoplankton and zooplankton. Holling (1973) has suggested that such diagrams may be useful in indicating the resilience of communities to environmental perturbations. At the low cyclopoid densities characteristically observed in acidic lakes and at low *Chaoborus* densities, zooplankton

Table 7-16. Densities of adult and copepodid D. minutus and Chaoborus instars I, II and III in Mountaintop Lake in 1977. Daily loss rates of D. minutus and inferred Chaoborus predation rates on D. minutus are included.

	D. minutus Density (animals L^{-1})	D. minutus[1] Loss Rate (animals $L^{-1}day^{-1}$)	Chaoborus Density (animals L^{-1})	Predation Rate[2] (D. minutus $Chaoborus^{-1}$ day^{-1})
May 11	20.6	–[3]	0.012	–[3]
25	58.1	–[3]	0.010	–[3]
June 10	64.6	–[3]	0.16	–[3]
23	53.0	0.90	0.19	5.0
July 5	45.3	0.64	0.13	3.9
19	13.0	2.30	0.49	7.4
Aug. 3	4.86	0.54	0.67	0.94
17	0.47	0.31	0.16[4]	0.76
Aug. 31	0.05	0.03	0.87	0.06
Sept. 15	0	0.003	0.81	<0.01

[1] calculated as the difference in densities between the indicated and the previous sampling date divided by the interval length.

[2] calculated as the loss rate divided by the average Chaoborus density over the interval.

[3] indicates negative loss rate, hence negative predation rate

[4] probably an underestimate of density, hence excluded from Fig. 7-42b

biomass increased so rapidly and to such an extent that the phytoplankton biomass was depressed almost to zero. However, when *Chaoborus* larvae were abundant, herbivorous zooplankton were virtually eliminated and phytoplankton biomass increased.

Planktonic fluctuations were much less marked in Labelle Lake. Fish predation probably limited *Chaoborus* densities. Cyclopoid predators were much more abundant than in Mountaintop Lake but Neill and Peacock (1980) have demonstrated that, unlike *Chaoborus*, cyclopoids are generally unable to decimate their prey.

Holling (1973) defined resilience as the persistence of system structure and relationships in the presence of an environmental perturbation. The elimination of fish and the reduction of cyclopoid densities accompanying the acidification of Mountaintop Lake has reduced the resilience of the herbivore community of the lake to added nutrients. The reduced resilience was manifest in either a crash or a large increase in grazer abundances depending on the temporal pattern of nutrient additions and its relation to *Chaoborus* life history.

While *Chaoborus* was the single most important determinant of herbivore densities one year after the onset of fertilization in Mountaintop Lake, this does not indicate, as suggested by Eriksson *et al*. (1980), that increased *Chaoborus* densities are responsible for some of the observed changes in herbivorous zooplankton communities in acidic lakes that have not been fertilized. It was not until *Chaoborus* densities were very high in the lake, about 1 animal L^{-1}, that their demographic control of zooplankton was evident. Neill (1981) has indicated that *Chaoborus* densities may be increased by 3-fold over typical levels, to levels about one-half of those at which a demographic effect on their prey was obvious in

Mountaintop Lake, without resulting in any significant changes in their prey populations. There is currently no available information on changes in Chaoborus populations following acidification of any North American lakes, or comparisons of Chaoborus densities in acidic and non-acidic North American lakes of similar trophic state. An assessment of the importance of Chaoborus in the zooplankton community of acidic lakes in North America cannot be made until such information exists.

E. Summary

1. Phosphorus was added to Middle and Hannah Lakes from 1975 to 1978 and from 1976 to 1978, respectively. Phosphorus (at much higher rates of supply) and nitrogen were added to non-acidic (pH~6.0) Labelle Lake from 1977 to 1978 and to acidic (pH~4.6) Mountaintop Lake from 1976 to 1978. Experimental additions provided >97% of the phosphorus supplied over the period of fertilization to Mountaintop and Labelle Lakes, 82-87% in Middle Lake and 79-82% in Hannah Lake.

2. Levels of TP increased in Middle and Hannah Lakes, but annual averages did not exceed 15 $\mu g\ L^{-1}$. Additions resulted in decreases of NO_3^- from 420 to 30 $\mu g\ L^{-1}$ in Middle Lake and from 520 to 90 $\mu g\ L^{-1}$ in Hannah Lake, and in large decreases in ratios of inorganic to organic nitrogen.

3. Phytoplankton biomass increased after additions of P. Chrysophytes were dominant in the spring in all years of fertilization, but dominant taxa in the summer were not predictable.

4. Zooplankton biomass was also increased by fertilization, but metal toxicity apparently limited the increase. Fertilization did not encourage the re-establishment of communities typically observed in uncontaminated Precambrian Shield lakes.

5. Phosphorus budgets for Mountaintop and Labelle Lakes indicated that phosphorus was transported to the sediments as rapidly in acidic as in non-acidic lakes, even at very high rates of fertilization.

6. Ratios of concentrations of N:P in Mountaintop and Labelle Lakes were 1.7-3.6 times higher than ratios of supply of N:P. This indicated that rates of loss of P from the water column were greater than rates of loss of N.
7. Differential uptake of NH_4^+ relative to NO_3^- was in part responsible for the decrease in epilimnetic pH that occurred over the summer in Mountaintop Lake. While pH normally increases in the euphotic zone of non-acidic lakes over the summer, in Mountaintop Lake it decreased, at one point to <4.0. In contrast, the pH of the hypolimnion increased to >6.0 at times of anoxia, most likely because of bacterial reduction of SO_4, NO_3 and ferric hydroxides. A portion of the generated alkalinity was re-entrained into the surficial waters at fall overturn.
8. Phytoplankton biomass increased substantially after fertilization in Mountaintop Lake, indicating that acidification of lakes will not prevent the development of the large phytoplankton standing stocks that characteristically accompany increased rates of nutrient supply. Temporal changes in species composition were much smaller in Mountaintop Lake than in Labelle Lake. A single species formed >90% of the community biomass for most of the ice-free season in each year.
9. Zooplankton densities increased in response to the increased phytoplankton food base in Labelle Lake. In the first year of fertilization in Mountaintop Lake, zooplankton densities increased to levels much higher than ever observed in Labelle Lake. Levels of herbivorous zooplankton were, in fact,

sufficiently high that their grazing activities reduced phytoplankton standing stocks to very low levels. Zooplankton densities decreased rapidly in the summer of the second year of fertilization in Mountaintop Lake and remained low (40 times lower than in the first year of fertilization) in the third fertilization season. Both the large increase in zooplankton biomass in the first year of fertization and the crash in the second and third years in Mountaintop Lake were attributable to predator prey interactions. In 1976 densities of invertebrate predators were 40 times lower than in Labelle Lake, and zooplankton densities increased substantially in an environment virtually free of predation. Phytoplankton populations were decimated in consequence. In the second year of fertilization in Mountaintop Lake, increased prey availability in the absence of fish allowed the development of very substantial populations of *Chaoborus*. *Chaoborus* reduced zooplankton densities to very low levels. Acidification indirectly reduced the resilience of the plankton communities of Mountaintop Lake to fertilization.

LIST OF FIGURES

Note: The following symbols have been used in this section.

Symbol	Meaning
△	first date, or dates, of addition of $Ca(OH)_2$
▲	first date, or dates, of addition of $Ca(OH)_2 + Ca(CO)_3$
◆	first date, or dates, of addition of P (to Middle and Hannah Lakes) and P and N (to Mountaintop and Labelle Lakes)

Fig. 7-1. Measured concentrations of TP in Middle Lake and predicted concentrations, including and excluding experimental additions of P (calculated as described in Chapter 6, Part B) from May, 1977 to December, 1979. Values are monthly averages or a concentration calculated once a month.

Fig. 7-2. Measured concentrations of TP in Hannah Lake and predicted concentrations including and excluding experimental additions of P (calculated as described in Chapter 6, Part B) from May, 1977 to December, 1979. Values are monthly averages or a concentration calculated once a month.

Fig. 7-3. Seasonal variations in the concentration of NO_2^--N plus NO_3^--N in Hannah Lake, 1973-1979.

Fig. 7-4. Seasonal variations in the concentration of NH_4^+-N in Hannah Lake, 1973-1979.

Fig. 7-5. Seasonal variations in the concentration of NH_4^+-N in Middle Lake, 1973-1979.

Fig. 7-6. Seasonal variations in the concentration of NO_2^--N plus NO_3^--N in Middle Lake, 1973-1979.

Fig. 7-7. Relationship of ice-free period average phytoplankton biomass of the S.E.S. lakes with pH and with TP. Mountaintop and Labelle Lakes not included. Data are from 1973-1978 in Middle(△), Clearwater(●) and Hannah(▲) Lakes, 1973-1979 in Lohi Lake(×), 1975-1978 for Nelson Lake, Station 1(○) and 1975-1977 for Station 4(◇), 1977 for Swan Lake(◆) and 1976 for Joe Lake(□).

Fig. 7-8. Cumulative phytoplankton biomass in Hannah Lake, 1973-1978.

Fig. 7-9. Cumulative phytoplankton biomass in Middle Lake, 1973-1978.

Fig. 7-10. Seasonal variations in dominant phytoplankton taxa in Hannah Lake, 1973-1978. Number in parentheses after class name represents proportional contribution of that class to total phytoplankton biomass over the indicated time interval with "1" being 0-10%; "2" being 10-20%, etc. Dominant genera and/or species within that class are listed.

Fig. 7-11. Seasonal variations in dominant phytoplankton taxa in Middle Lake, 1973-1978. Numbers in parentheses as in Fig. 7-10.

Fig. 7-12. Seasonal variations in densities of *B. longirostris*, *C. sphaericus* and *C. vernalis* in Hannah Lake, 1973-1978.

Fig. 7-13. Seasonal variations in densities of *B. longirostris* and *C. sphaericus* in Middle Lake, 1973-1978.

Fig. 7-14. Seasonal variations in densities of dominant cyclopoid copepods in Middle Lake, 1973-1978.

Fig. 7-15. Thickness of epilimnion in Mountaintop Lake, 1976-1978.

Fig. 7-16. Seasonal variations in temperature at a depth of 8 m (1 m above the bottom) in Mountaintop Lake, 1976-1978.

Fig. 7-17. Seasonal variations in Secchi transparency in Mountaintop Lake, 1976-1978.

Fig. 7-18. Oxygen isopleth maps for Mountaintop Lake, 1976-1979.

Fig. 7-19. Oxygen isopleth maps for Labelle Lake, 1977-1979.

Fig. 7-20. Vertical profiles of concentrations of Fe in Mountaintop Lake on four dates in 1979.

Fig. 7-21. Seasonal variations in concentrations of TP and three nitrogen fractions in Mountaintop Lake, 1976-1979.

Fig. 7-22. Seasonal variations in concentrations of TP and three fractions of nitrogen in Labelle Lake, 1977-1978.

Fig. 7-23. Measured pH values of volume-weighted, whole lake composite samples from Mountaintop Lake, 1976-1978. 1979 data are also included, although only five measurements were made.

Fig. 7-24. Isopleth diagrams of pH in Mountaintop Lake, 1977-1979.

Fig. 7-25. Vertical profiles of DIC (mg L^{-1} of C) on three dates in 1979 in Mountaintop Lake.

Fig. 7-26. Isopleth diagrams of alkalinity in Mountaintop Lake, 1978 to 1979.

Fig. 7-27. Isopleth diagrams of pH in Labelle Lake, 1977-1978.

Fig. 7-28. Seasonal changes in calculated generation of acid from differential NH_4^+ and NO_3^- utilization in Mountaintop Lake. "Δ" represents the difference between predicted and measured concentration of the indicated fraction of nitrogen. Negative values indicate acid consumption.

Fig. 7-29. Changes in NO_3^--N in whole lake composite samples over the late winter and spring of 1977 and 1978 in Mountaintop Lake.

Fig. 7-30. Seasonal variations in concentration of chlor a in Mountaintop Lake, 1976-1978.

Fig. 7-31. Cumulative phytoplankton biomass in Mountaintop Lake, 1976-1978.

Fig. 7-32. Relationship between ice-free period average phytoplankton biomass from Mountaintop and Labelle Lakes with pH and TP.

Fig. 7-33. Seasonal variations in dominant phytoplankton taxa in Mountaintop Lake, 1976-1978. Numbers in parentheses as in Fig. 7-10.

Fig. 7-34. Cumulative phytoplankton biomass in Labelle Lake, 1977-1978.

Fig. 7-35. Seasonal variations in dominant phytoplankton taxa in Labelle Lake, 1977-1978. Numbers in parentheses as in Fig. 7-10.

Fig. 7-36. Cumulative biomass of crustacean zooplankton in Mountaintop Lake, 1976-1978.

Fig. 7-37. Contribution of Rotifera and Crustacea to total zooplankton biomass in Mountaintop Lake, 1976-1978.

Fig. 7-38. Cumulative biomass of crustacean zooplankton in Labelle Lake, 1977-1978.

Fig. 7-39. Seasonal variations in densities of dominant calanoid copepods in Labelle Lake, 1977-1978.

Fig. 7-40. Seasonal variations in contributions of Rotifera and Crustacea to total zooplankton biomass in Labelle Lake, 1977-1978.

Fig. 7-41. Seasonal changes in densities of a. rotifers, b. Chaoborus americanus and c. Diaptomus minutus in Mountaintop Lake from 1976 to 1978.

Fig. 7-42. Head capsule lengths of larval instars of Chaoborus americanus in Mountaintop Lake. Vertical bars are the standard deviation about the mean represented by the solid circle. Number of measurements are indicated in parentheses.

Fig. 7-43 Average (June to September) vertical distribution of Chaoborus americanus (not corrected for morphometry) in Mountaintop Lake. Average temperature profiles calculated over the same time period are also indicated.

Fig. 7-44. Phase-plane diagram of phytoplankton and zooplankton biomass and Chaoborus americanus density in Mountaintop Lake, 1976, 1977 and 1978. Arrows indicate direction of temporal trajectories. Values are consecutive monthly averages for May (M), June (J), July (J), August (A), September (S), October (O) and November (N). Hatching indicates location of a trajectory only, it does not delineate a response surface.

Fig.7-1

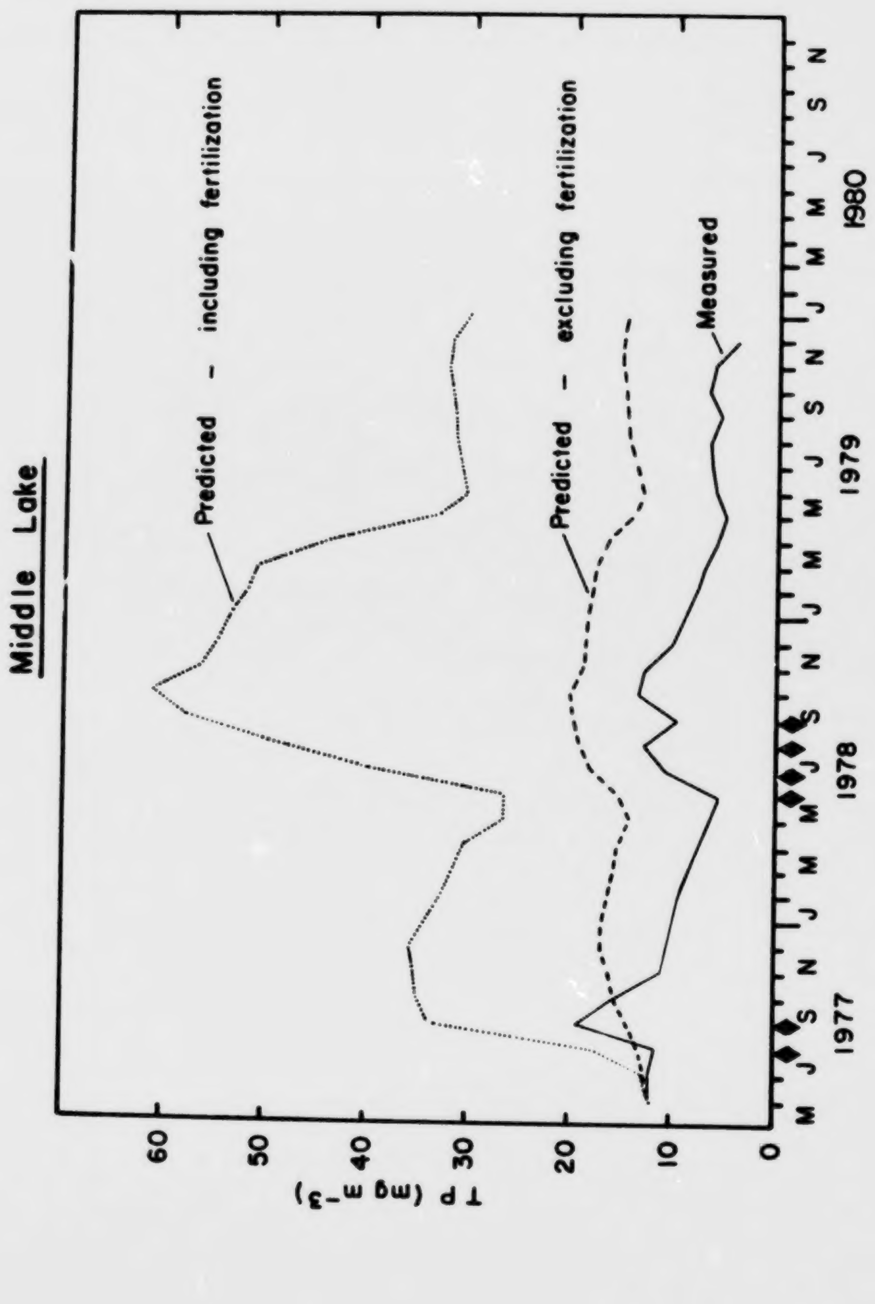

Middle Lake
Predicted - including fertilization
Predicted - excluding fertilization
Measured
T P (mg m⁻³)
0
10
20
30
40
50
60
M
J
S
N
J
M
M
J
S
N
J
M
M
J
S
N
J
M
M
J
S
N
1977
1978
1979
1980

Fig.7-2

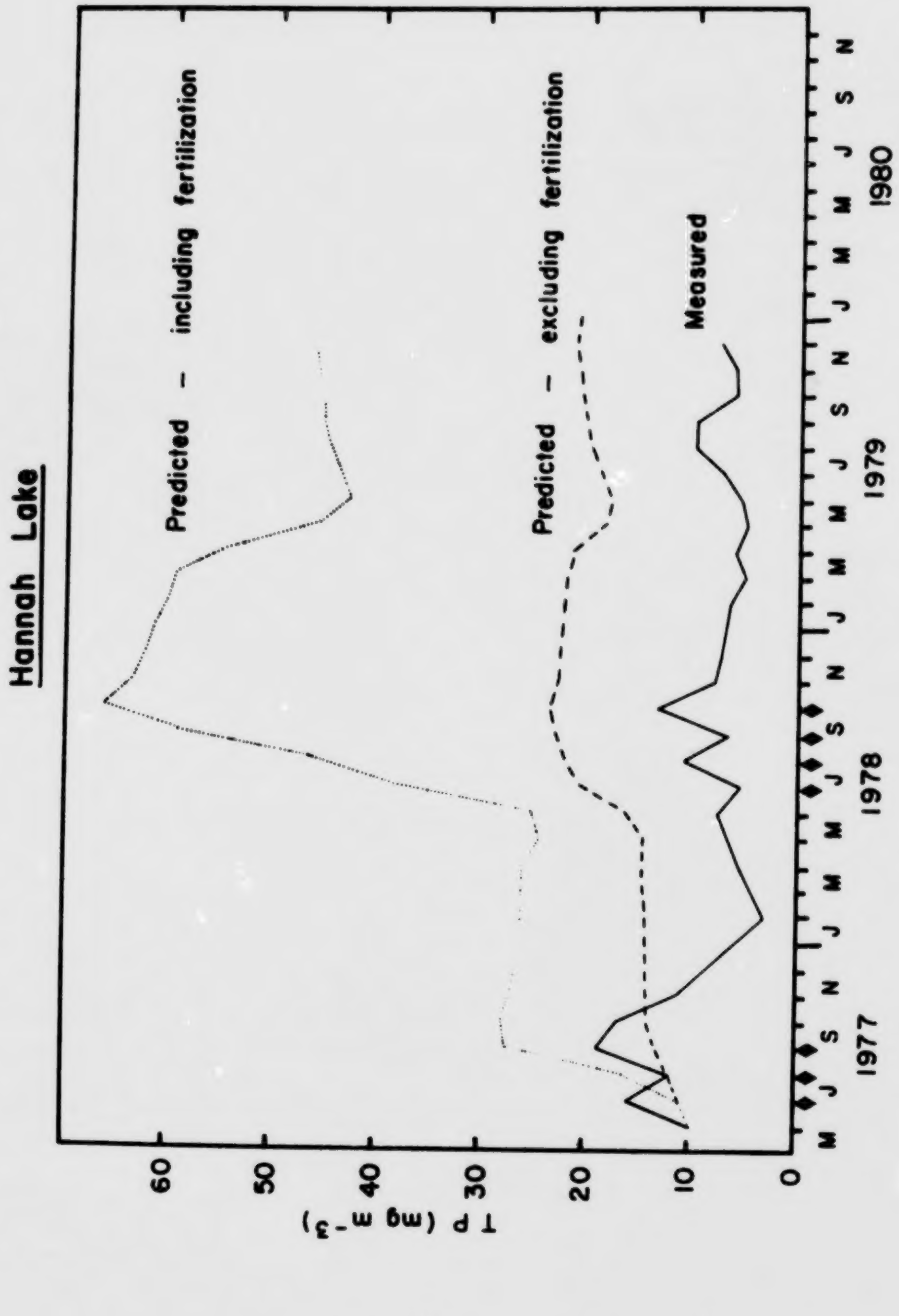

Hannah Lake
Predicted - including fertilization
Predicted - excluding fertilization
Measured
T P (mg m-3)
0
10
20
30
40
50
60
M J J S N J M M J J S N J M M J J S N J M M J J S N
1977
1978
1979
1980

Fig.7-3

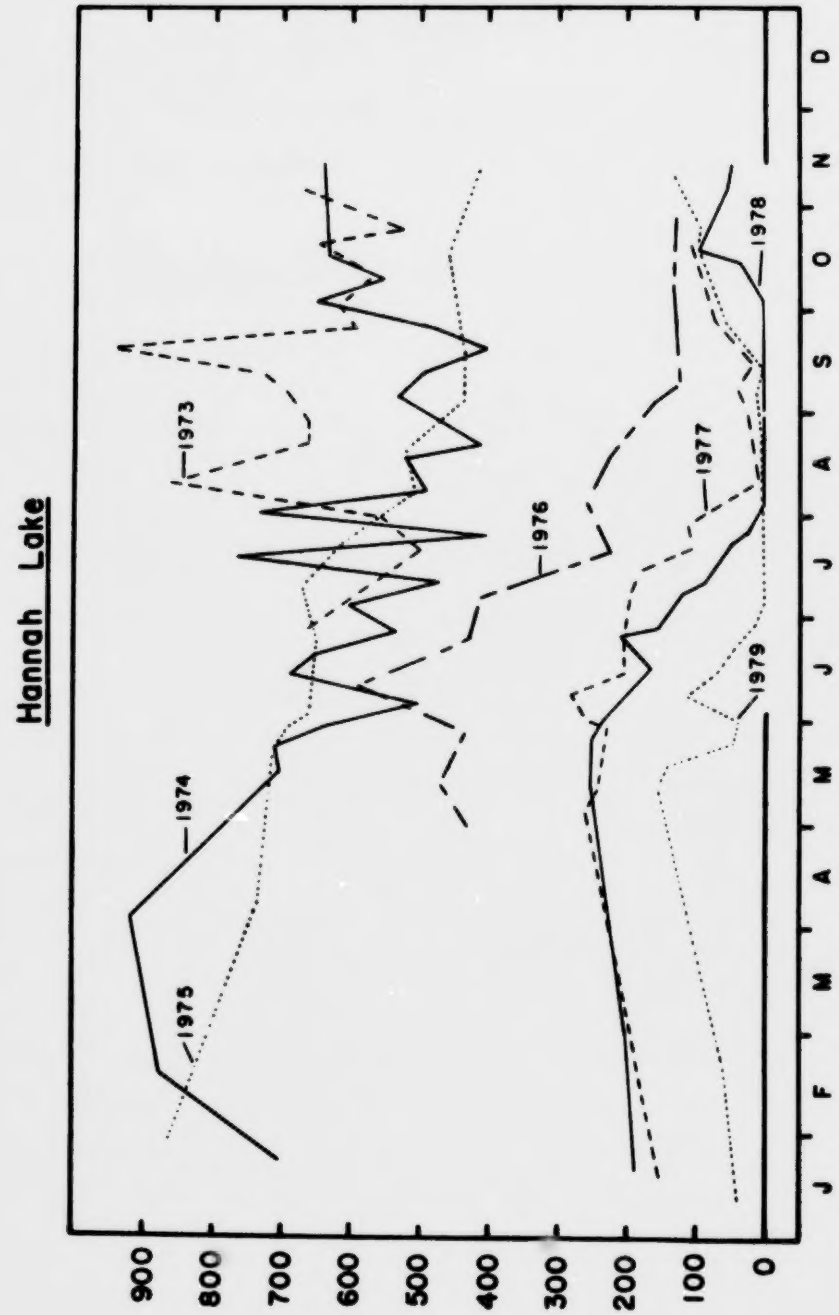

Hannah Lake
NO$_2$-N + NO$_3$-N (mg m^{-3})
900
800
700
600
500
400
300
200
100
0
J
F
M
A
M
J
J
A
S
O
N
D
1973
1974
1975
1976
1977
1978
1979

Fig.7-4

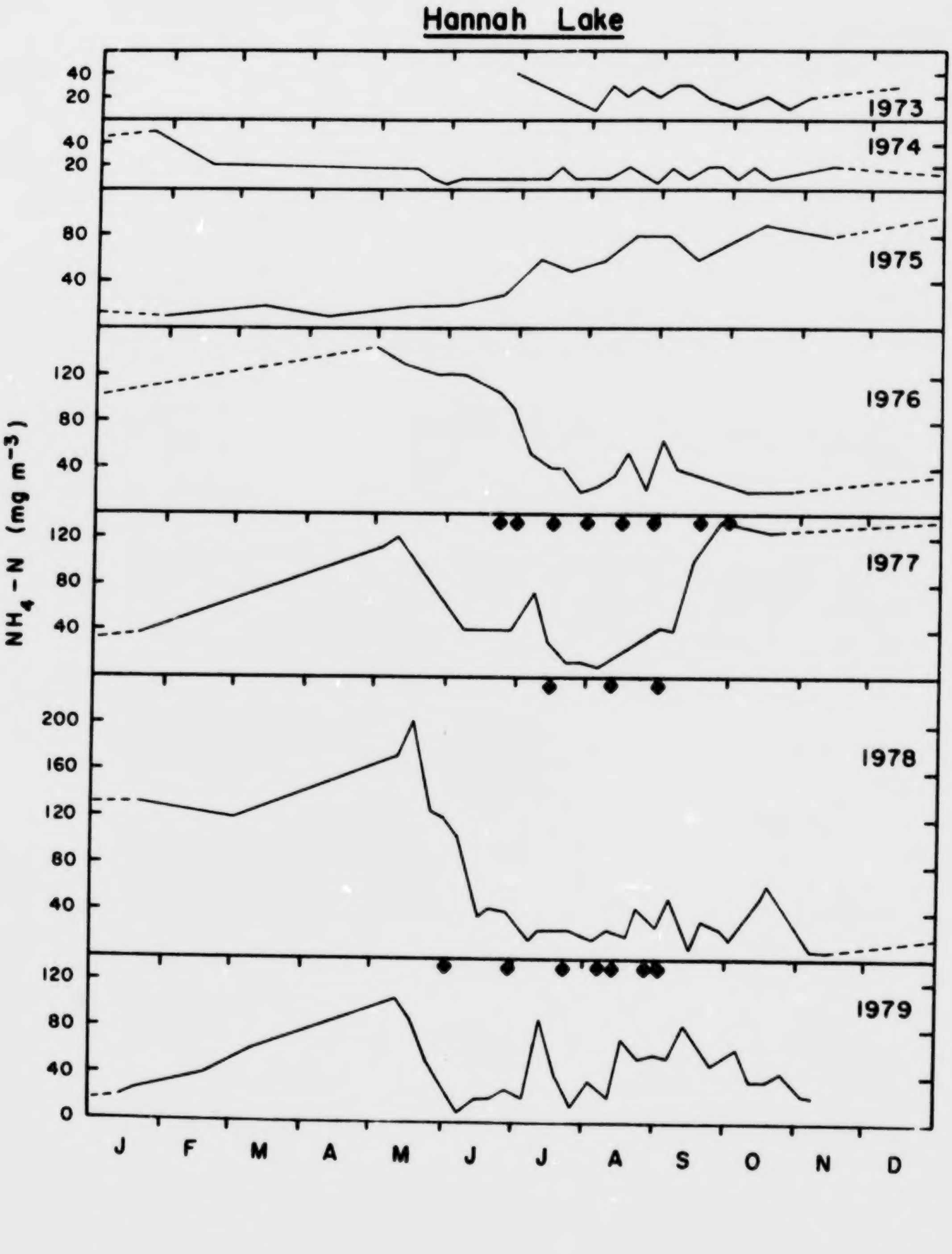

Hannah Lake
1973
1974
1975
1976
1977
1978
1979
NH_4-N (mg m^{-3})
40
20
40
20
80
40
120
80
40
120
80
40
200
160
120
80
40
120
80
40
0
J
F
M
A
M
J
J
A
S
O
N
D

Fig.7-5

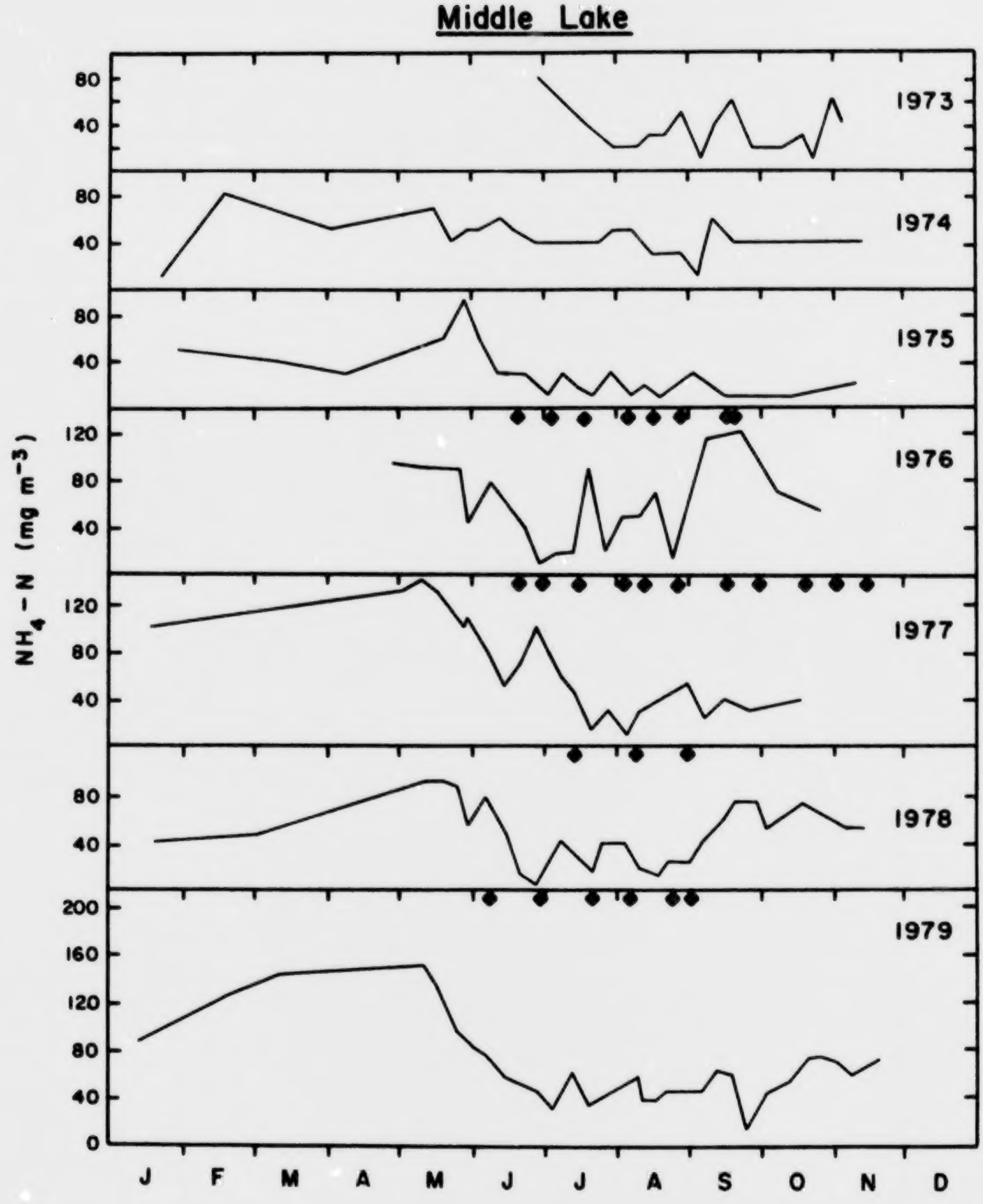
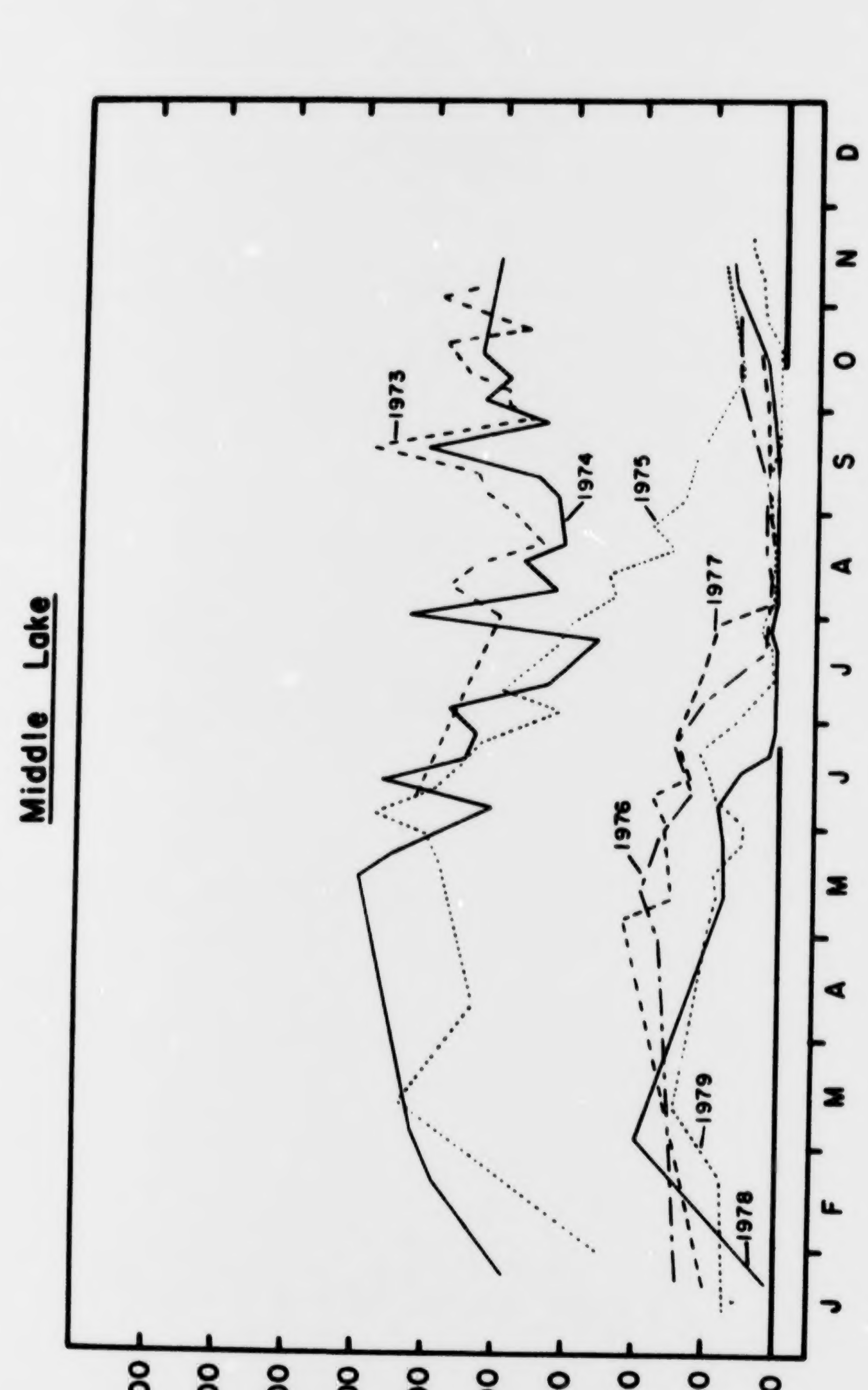

Middle Lake
NH$_4$ - N (mg m^{-3})
1973
1974
1975
1976
1977
1978
1979
80
40
120
160
200
0
J
F
M
A
M
J
J
A
S
O
N
D

Fig.7-6



Middle Lake

Fig.7-7

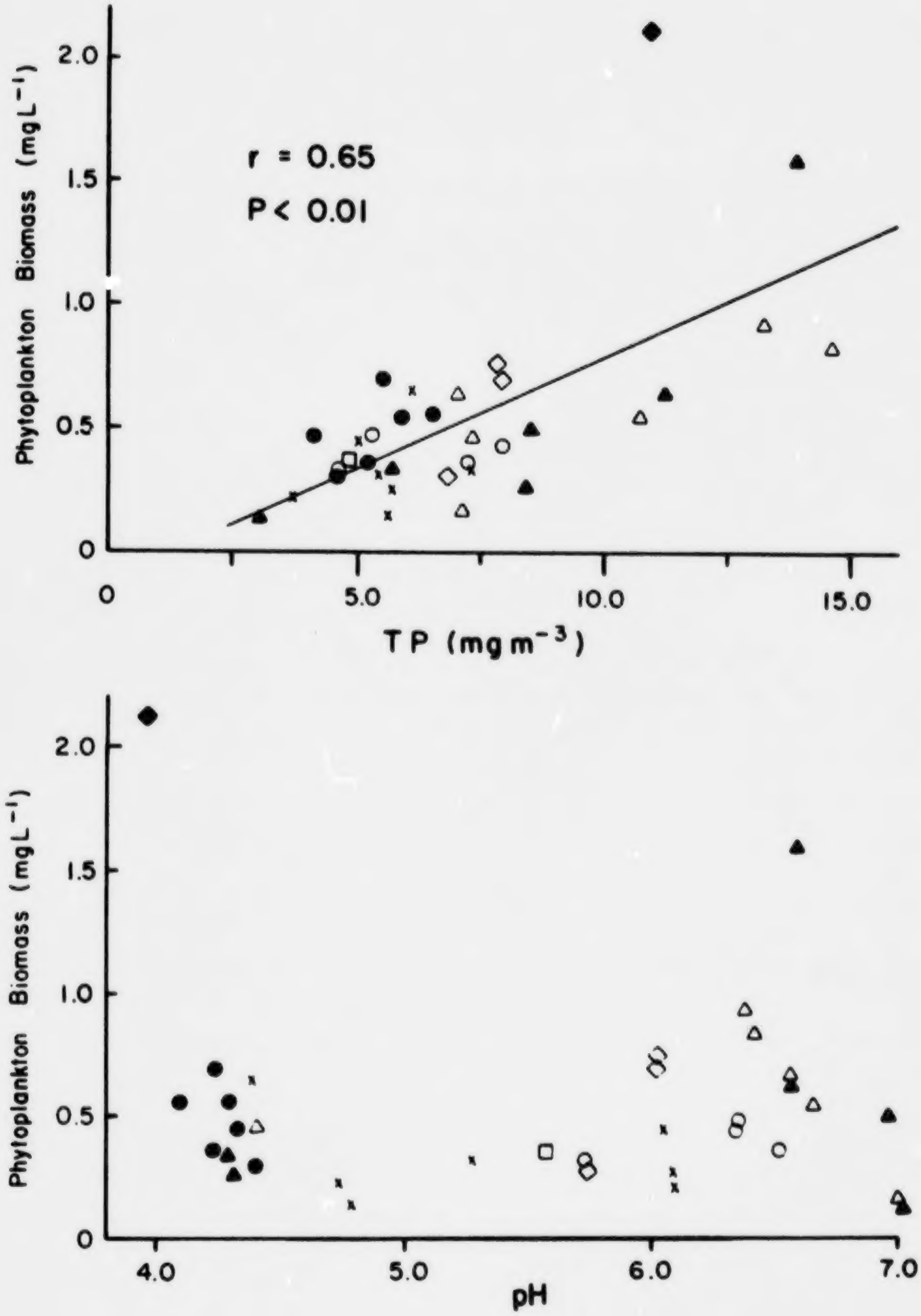

Phytoplankton Biomass (mgL⁻¹)
2.0
1.5
1.0
0.5
0
r = 0.65
P< 0.01
0
5.0
10.0
15.0
TP (mg m⁻³)
Phytoplankton Biomass (mgL⁻¹)
2.0
1.5
1.0
0.5
0
4.0
5.0
6.0
7.0
pH

Fig.7-8

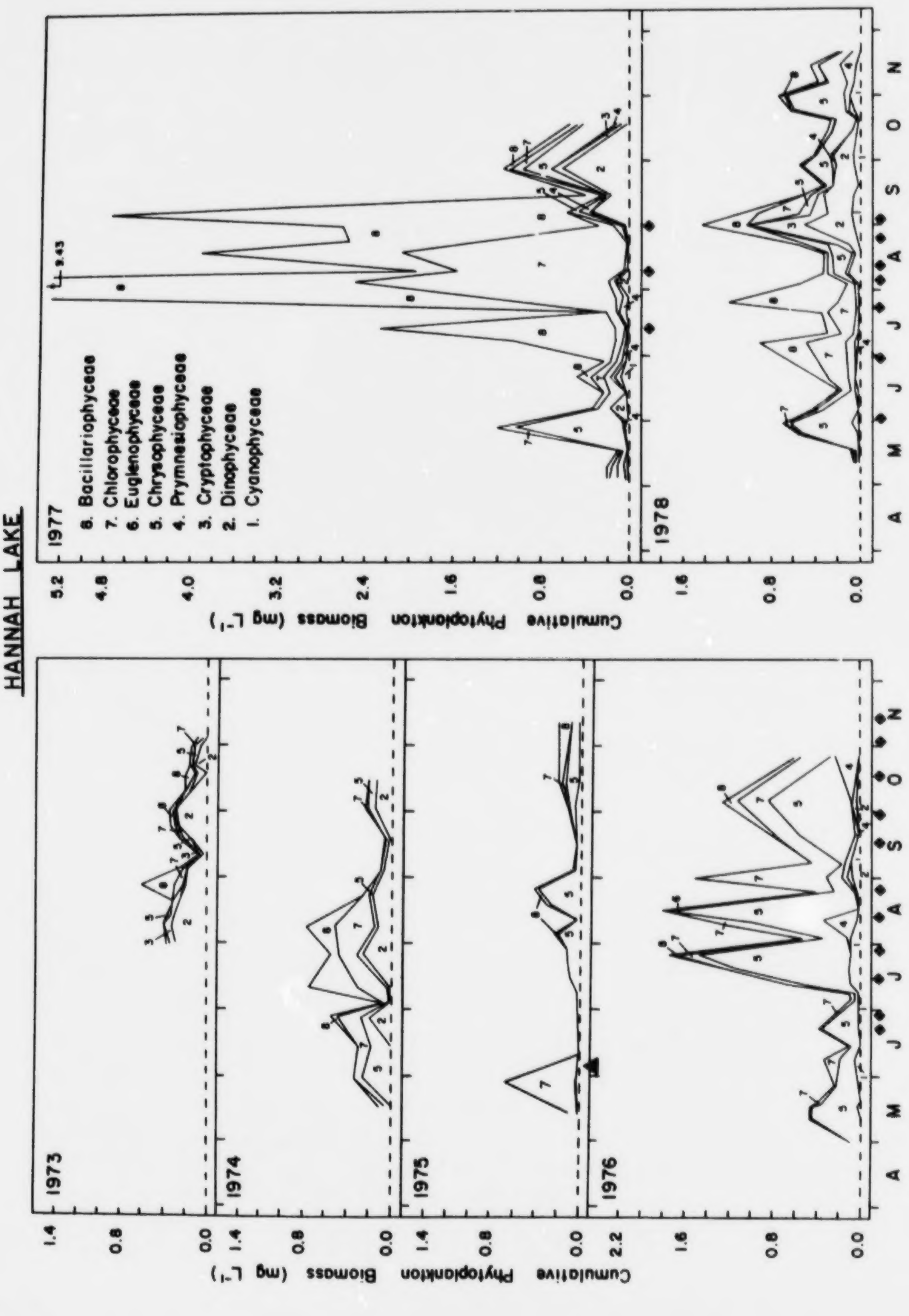

HANNAH LAKE
Cumulative Phytoplankton Biomass (mg L⁻¹)
1973
1974
1975
1976
1977
1978
8. Bacillariophyceae
7. Chlorophyceae
6. Euglenophyceae
5. Chrysophyceae
4. Prymnesiophyceae
3. Cryptophyceae
2. Dinophyceae
1. Cyanophyceae
9.43
A
M
J
J
A
S
O
N
0.0
0.8
1.4
1.6
2.2
2.4
3.2
4.0
4.8
5.2

Fig.7-9

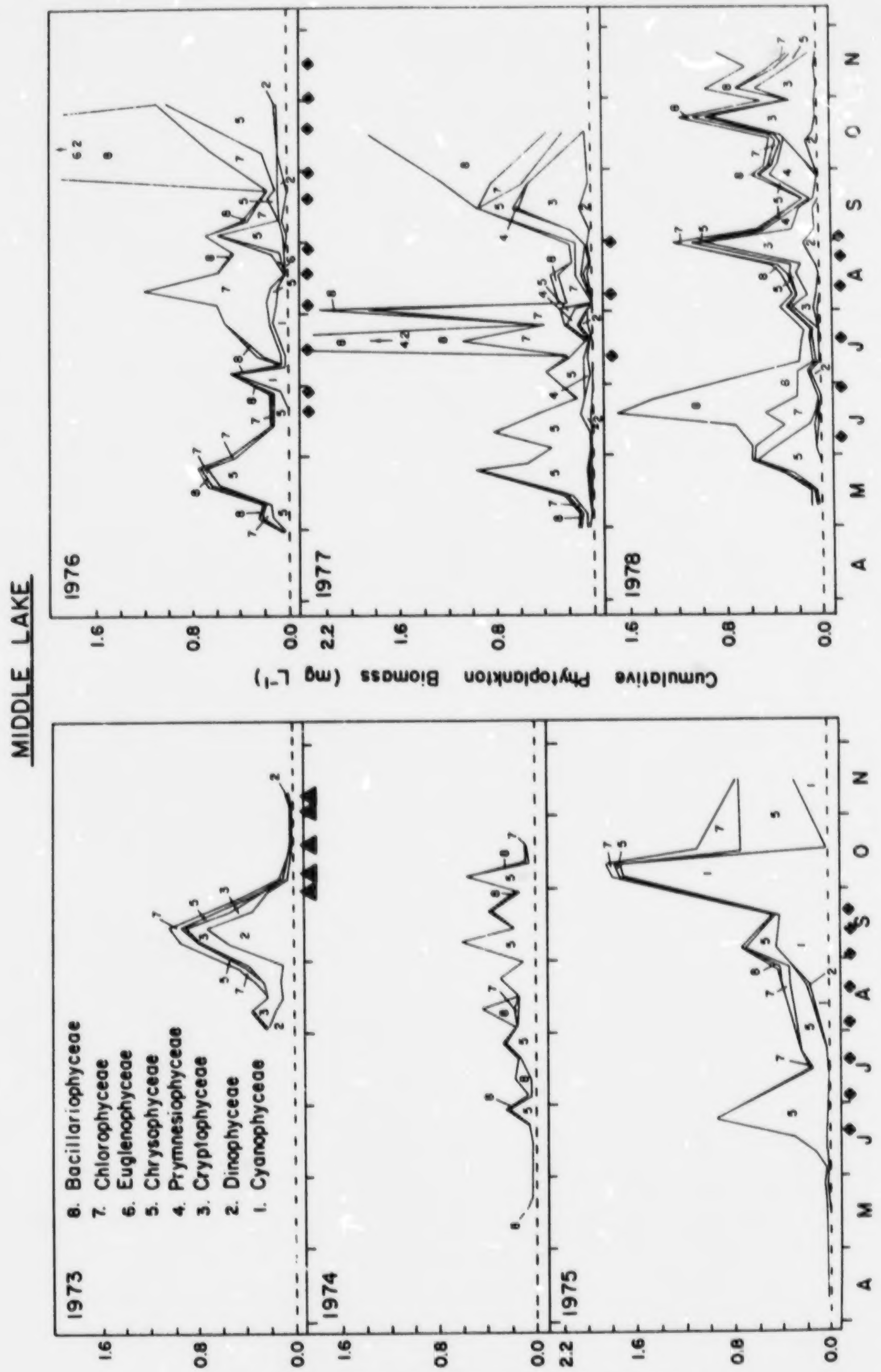

MIDDLE LAKE
8. Bacillariophyceae
7. Chlorophyceae
6. Euglenophyceae
5. Chrysophyceae
4. Prymnesiophyceae
3. Cryptophyceae
2. Dinophyceae
1. Cyanophyceae
1973
1974
1975
1976
1977
1978
Cumulative Phytoplankton Biomass (mg L⁻¹)
0.0
0.8
1.6
2.2
A
M
J
J
A
S
O
N

Fig.7-10

HANNAH LAKE

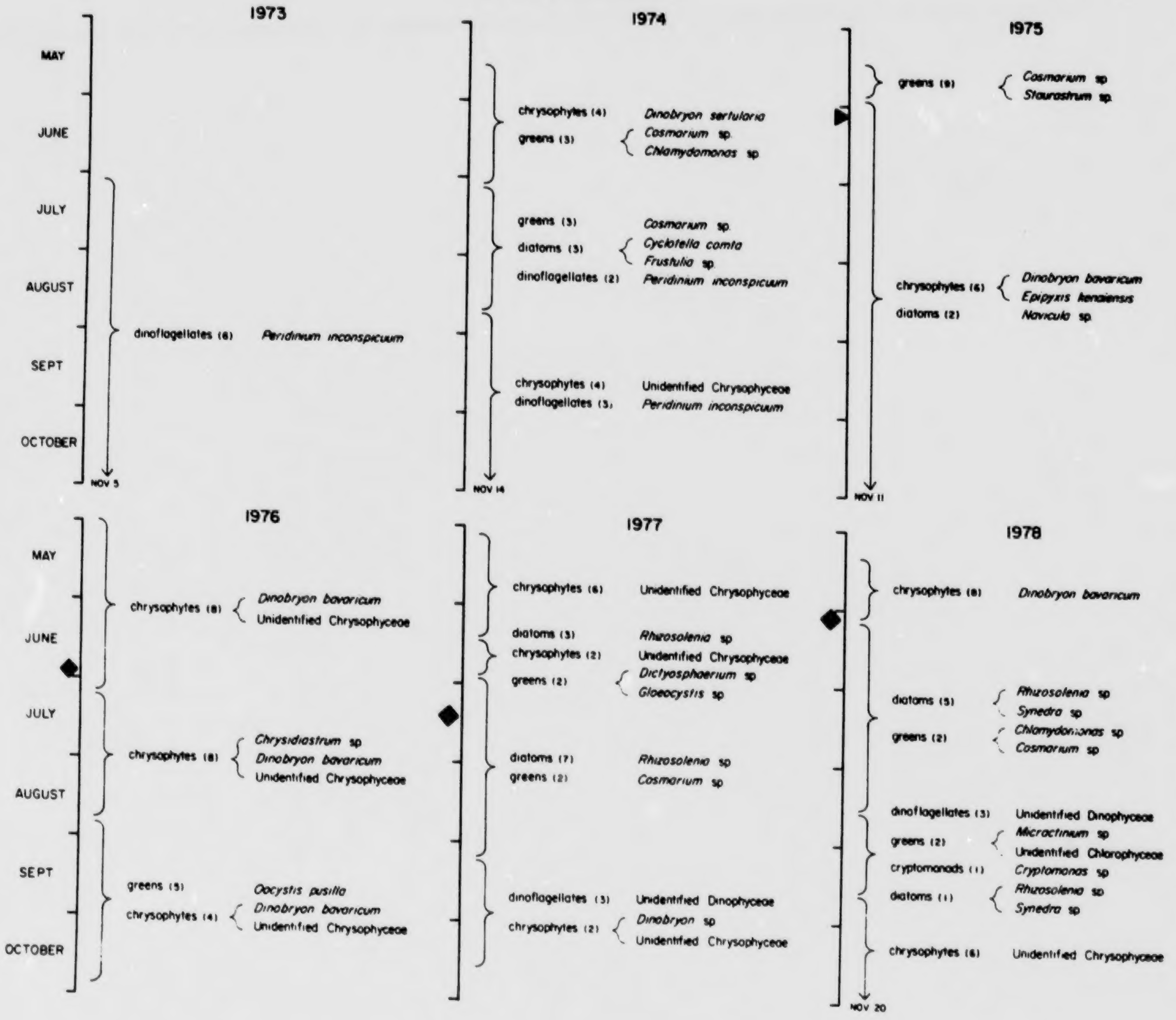


Fig.7-11

MIDDLE LAKE

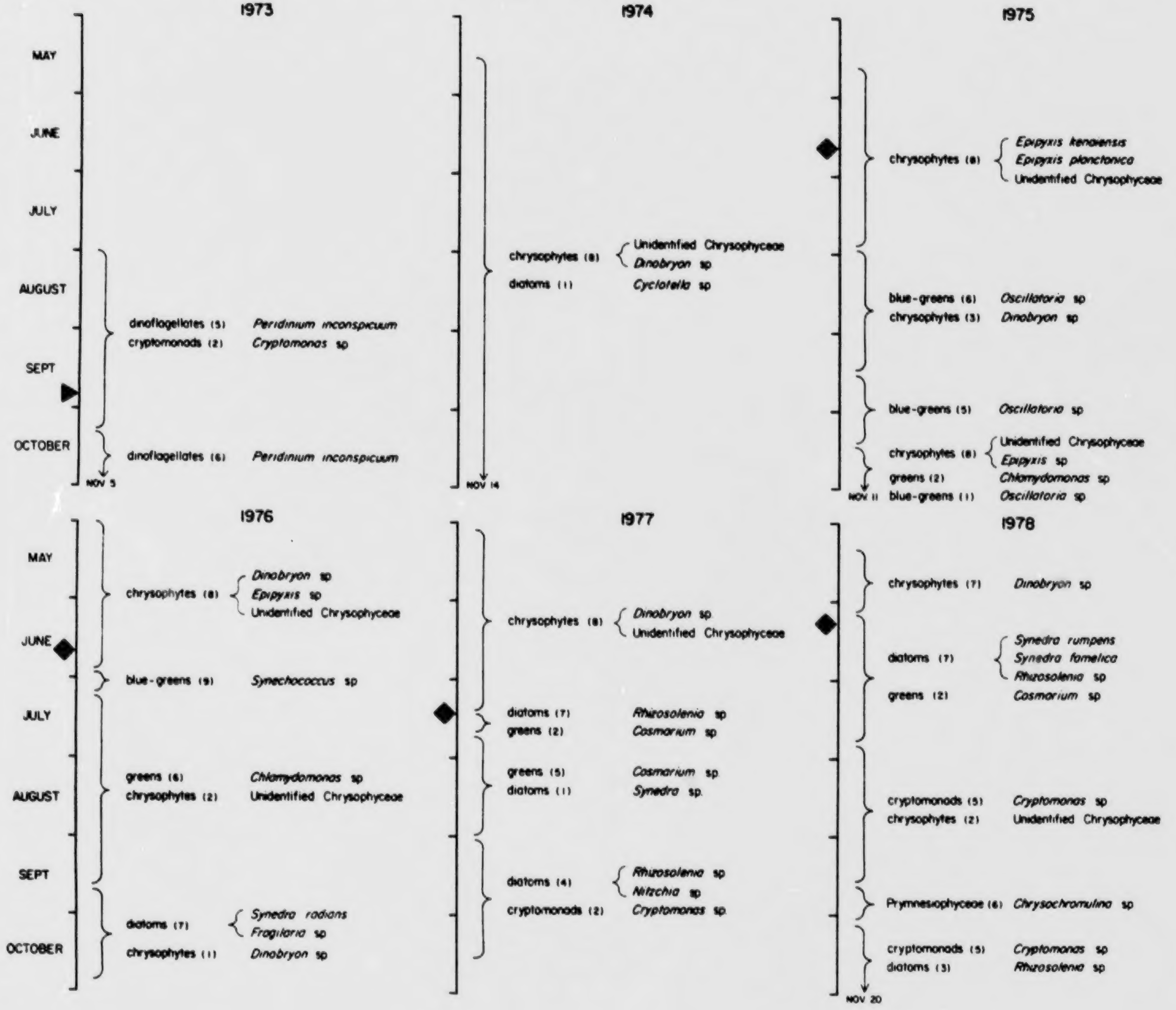


Fig.7-12

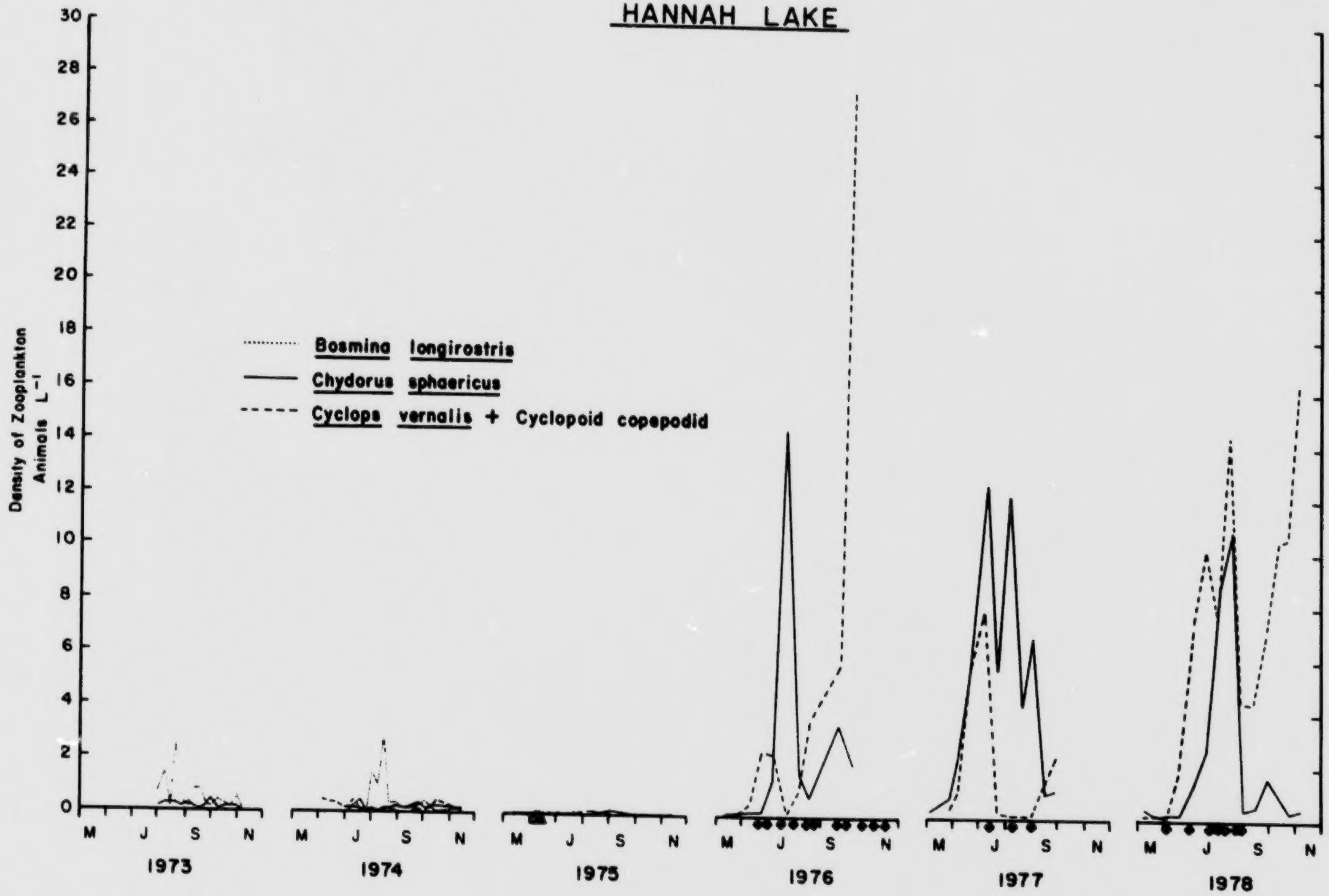

HANNAH LAKE
Density of Zooplankton Animals L⁻¹
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
Bosmina longirostris
Chydorus sphaericus
Cyclops vernalis + Cyclopoid copepodid
M J S N
1973
1974
1975
1976
1977
1978

Fig.7-13

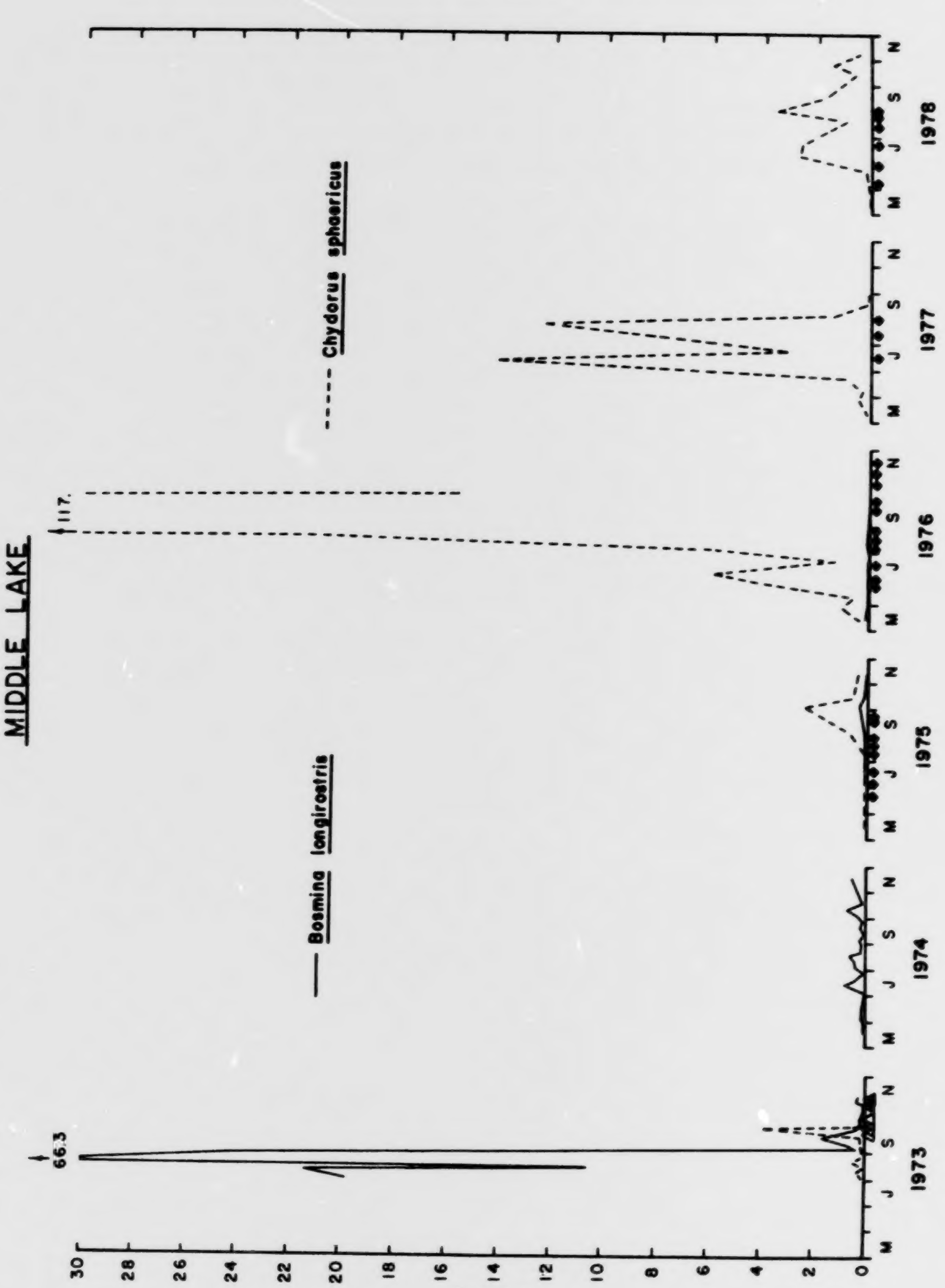

MIDDLE LAKE
— Bosmina longirostris
---- Chydorus sphaericus
66.3
117.
Density of Zooplankton
Animals L⁻¹
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
M
J
S
N
1973
1974
1975
1976
1977
1978

Fig.7-14

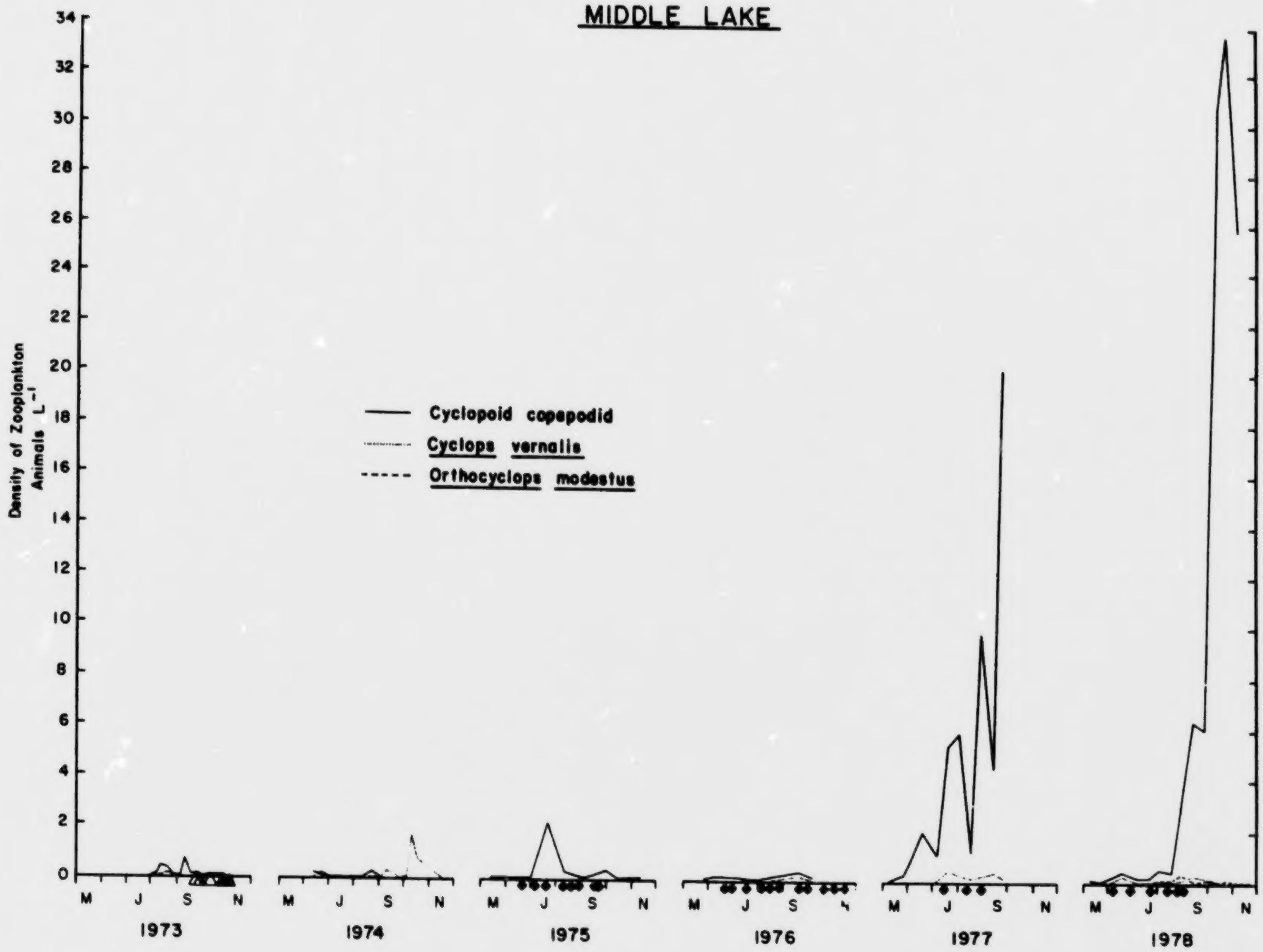

MIDDLE LAKE
Density of Zooplankton
Animals L^{-1}
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
Cyclopoid copepodid
Cyclops vernalis
Orthocyclops modestus
M
J
S
N
1973
1974
1975
1976
1977
1978

Fig.7-15

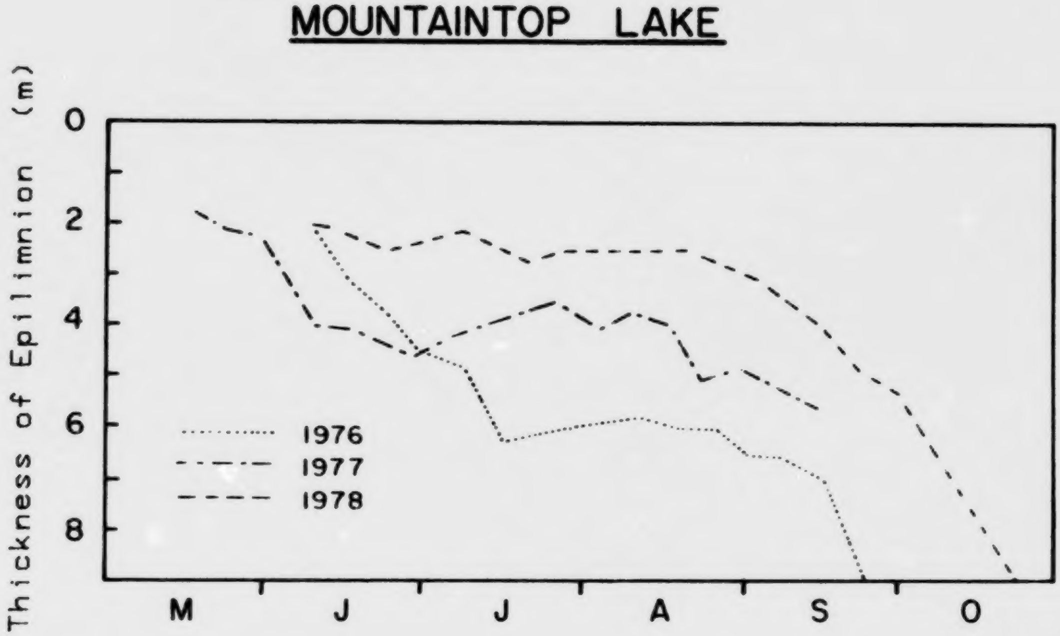

MOUNTAINTOP LAKE

Fig.7-16

MOUNTAINTOP LAKE

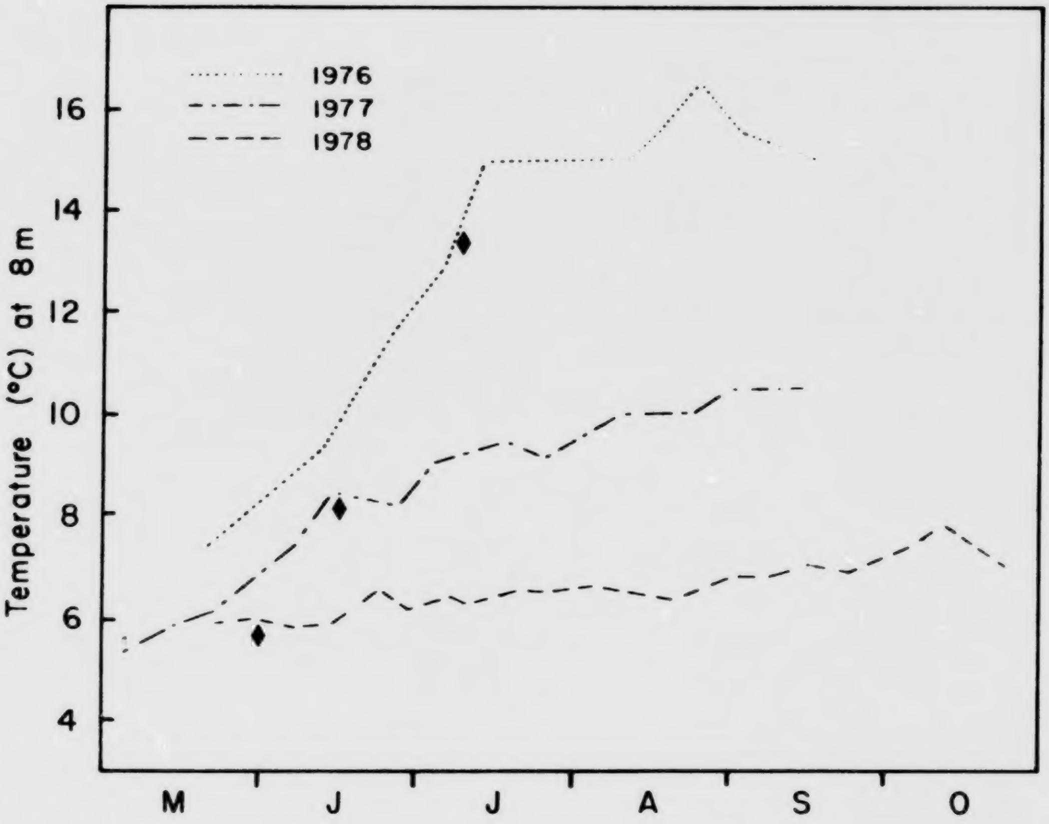
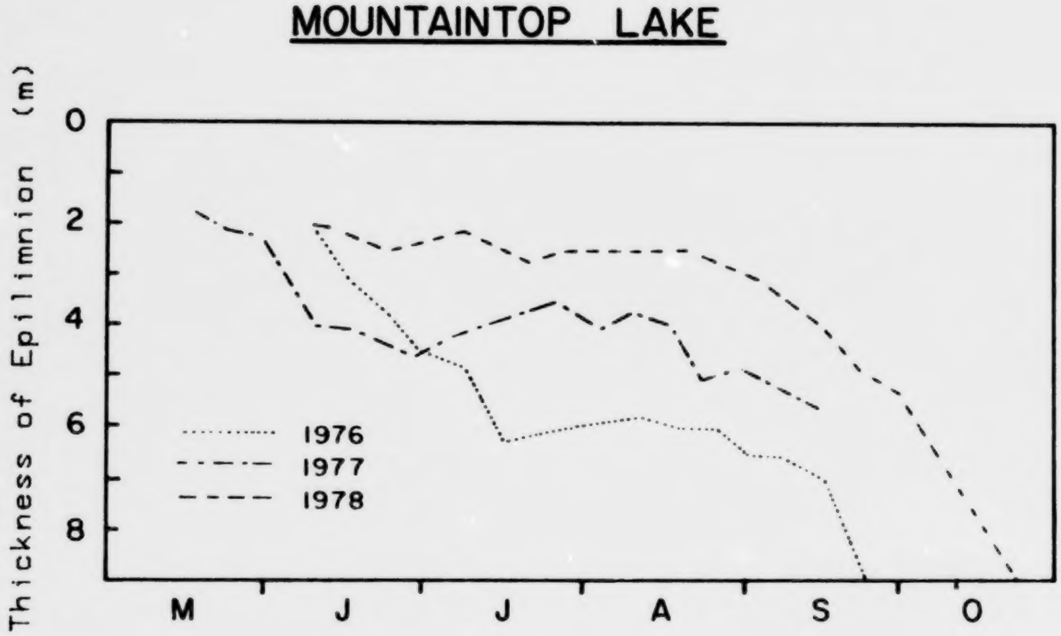


Fig.7-15



MOUNTAINTOP LAKE

Fig.7-16

MOUNTAINTOP LAKE

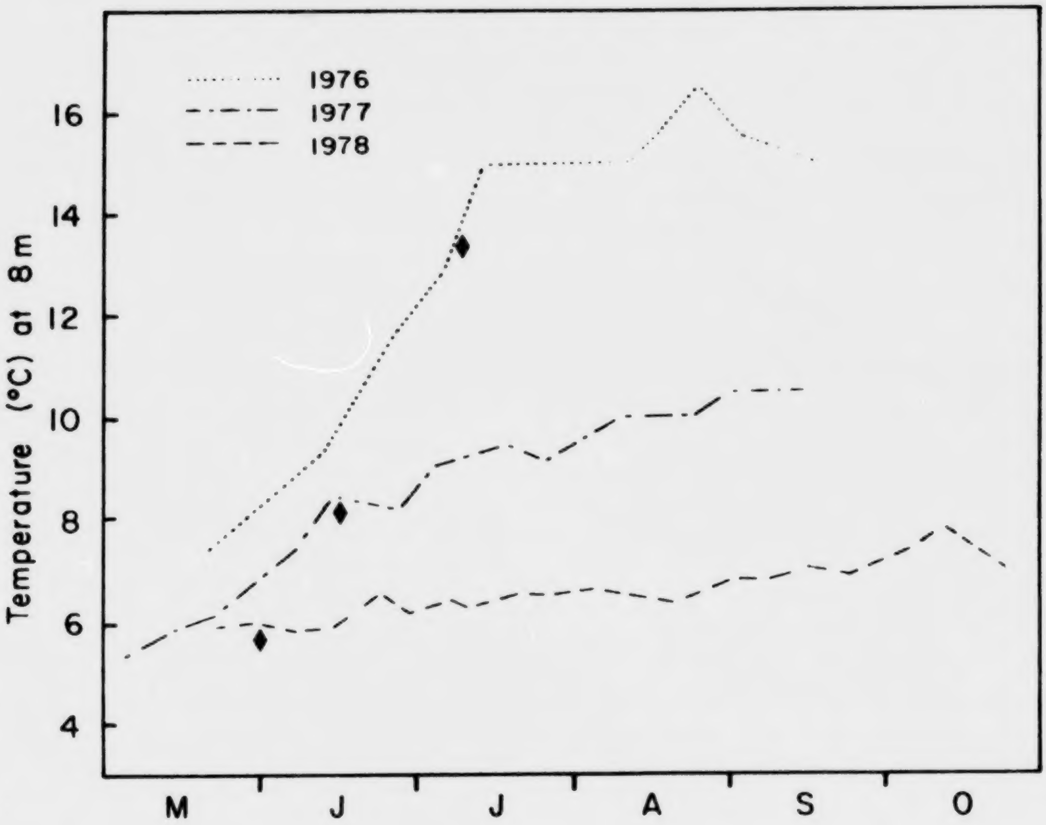


Fig.7-17

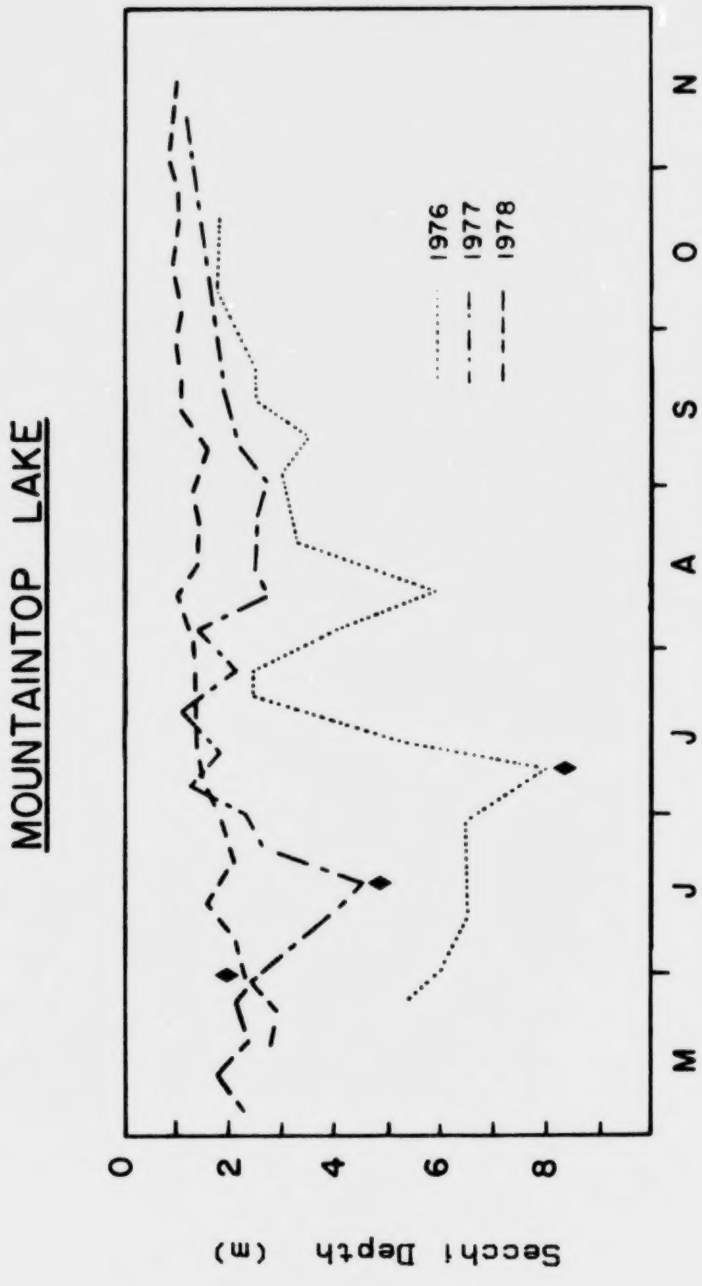
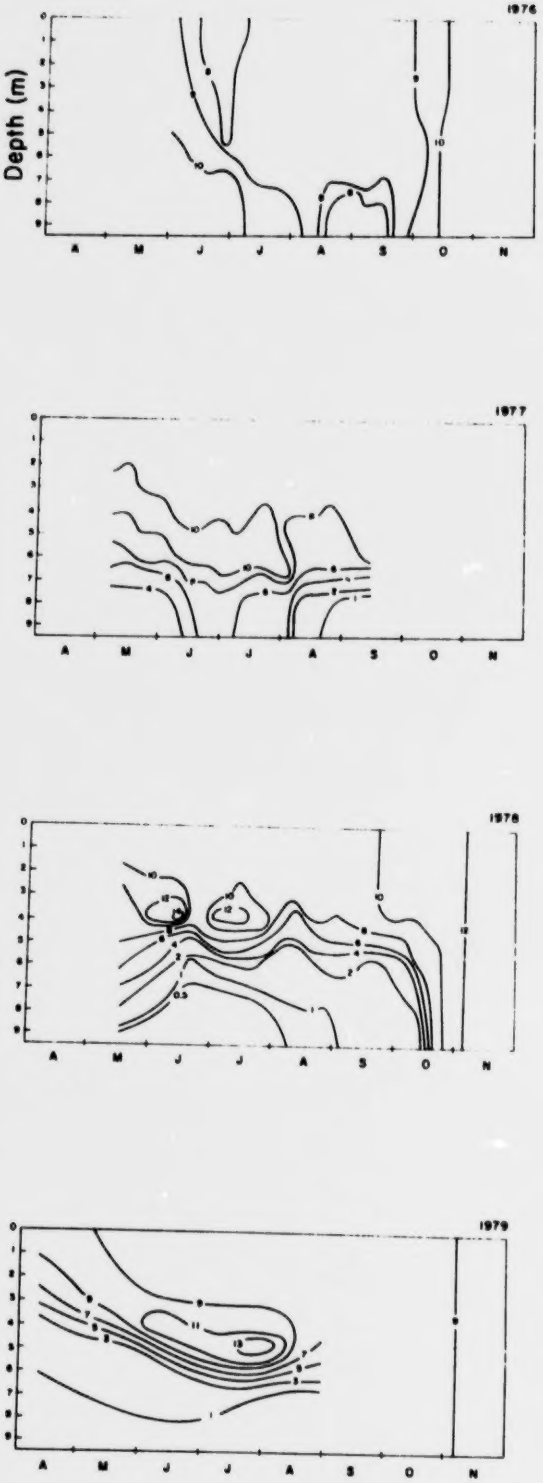

MOUNTAINTOP LAKE
Secchi Depth (m)
0
2
4
6
8
M
J
J
A
S
O
N
1976
1977
1978

Fig.7-18



MOUNTAINTOP LAKE

Oxygen (mg L^{-1}) isopleth maps

Fig.7-19

LABELLE LAKE

Oxygen (mg L^{-1}) isopleth maps

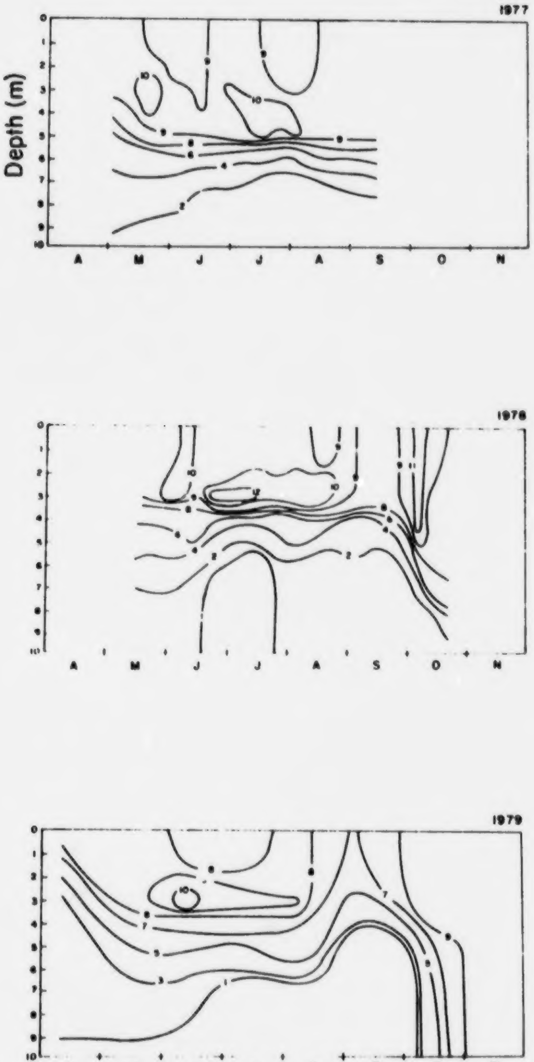


Fig.7-20

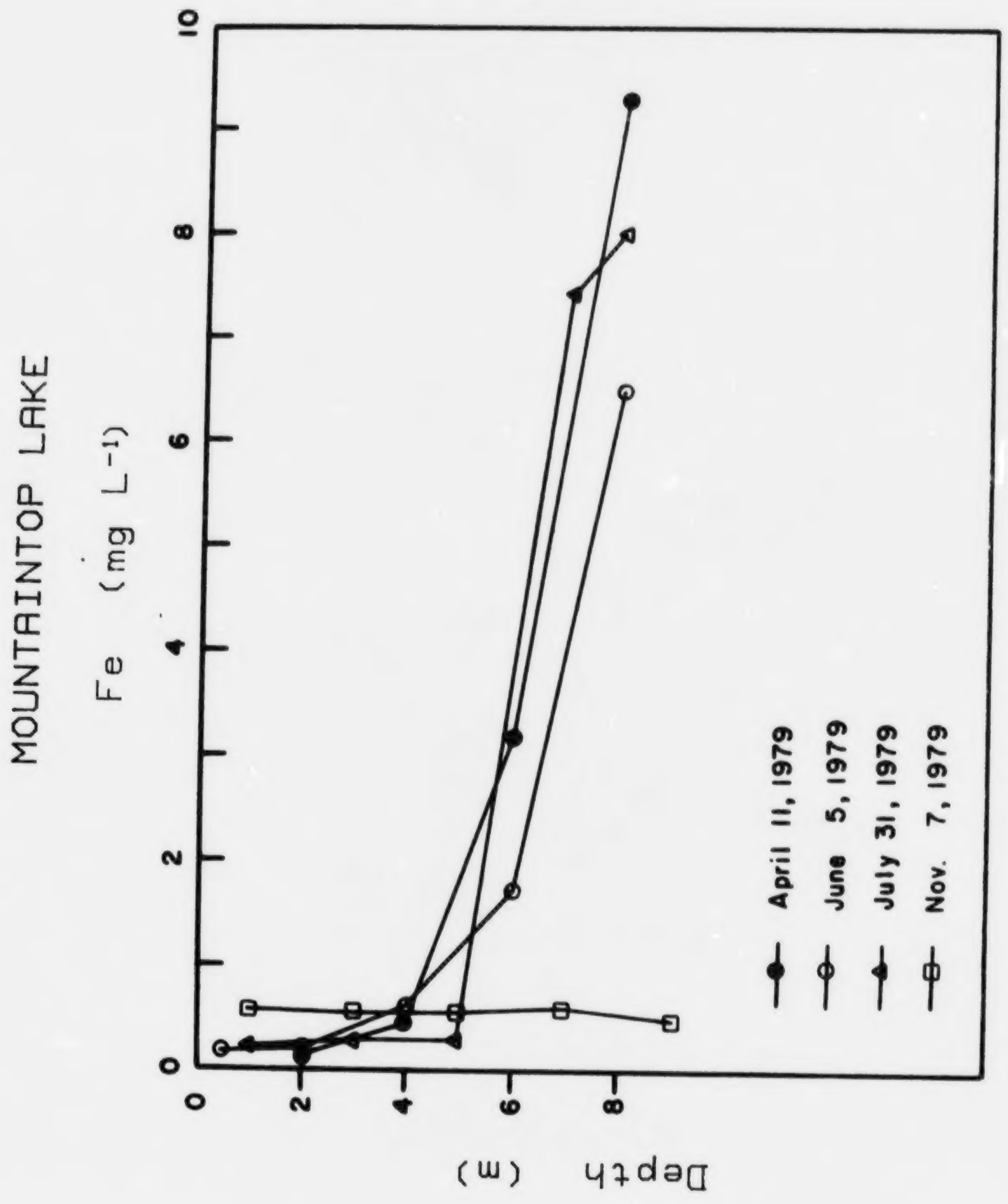

MOUNTAINTOP LAKE
Fe (mg L^{-1})
0
2
4
6
8
10
Depth (m)
0
2
4
6
8
April 11, 1979
June 5, 1979
July 31, 1979
Nov. 7, 1979

Fig.7-21

MOUNTAINTOP LAKE

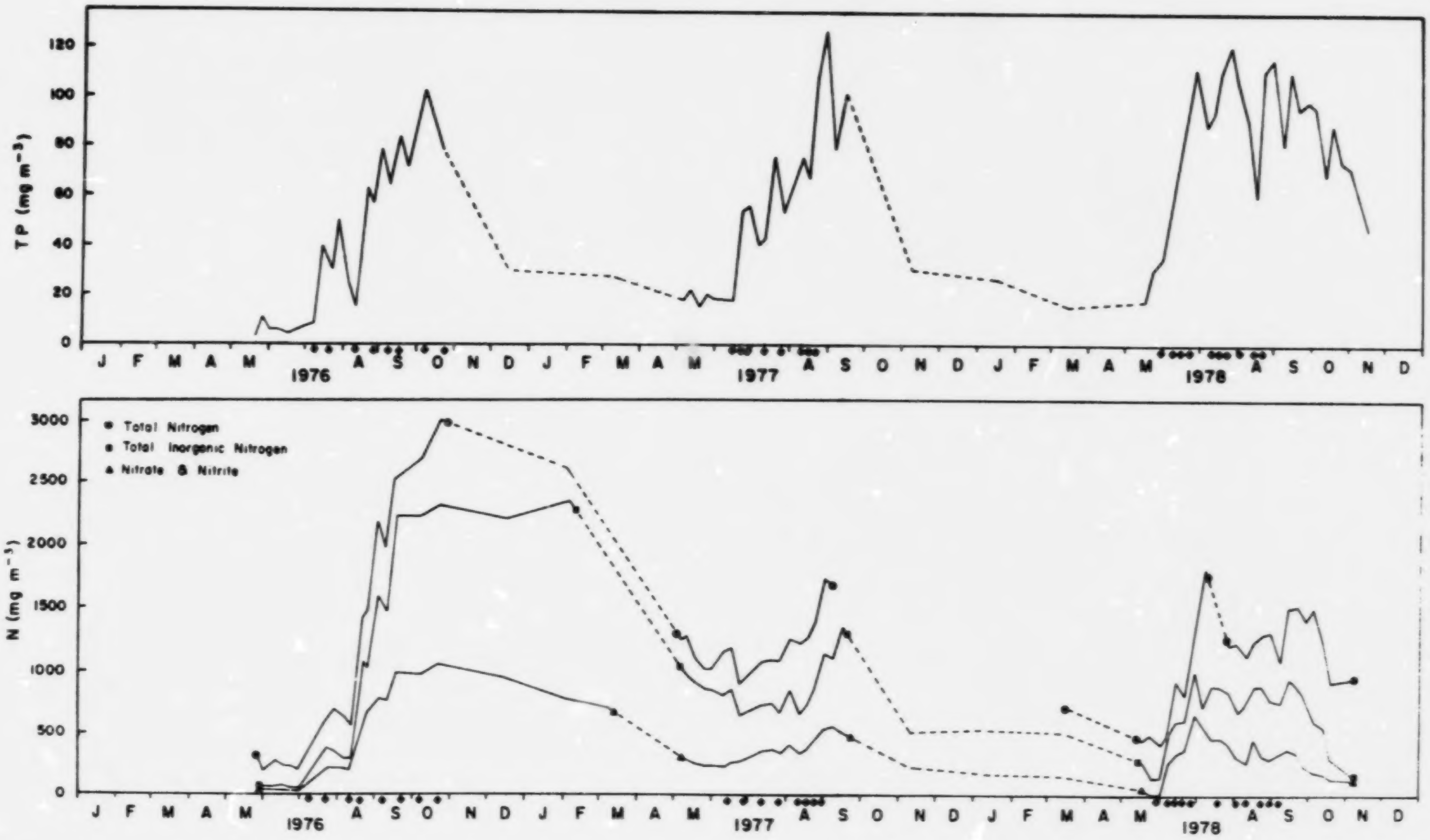
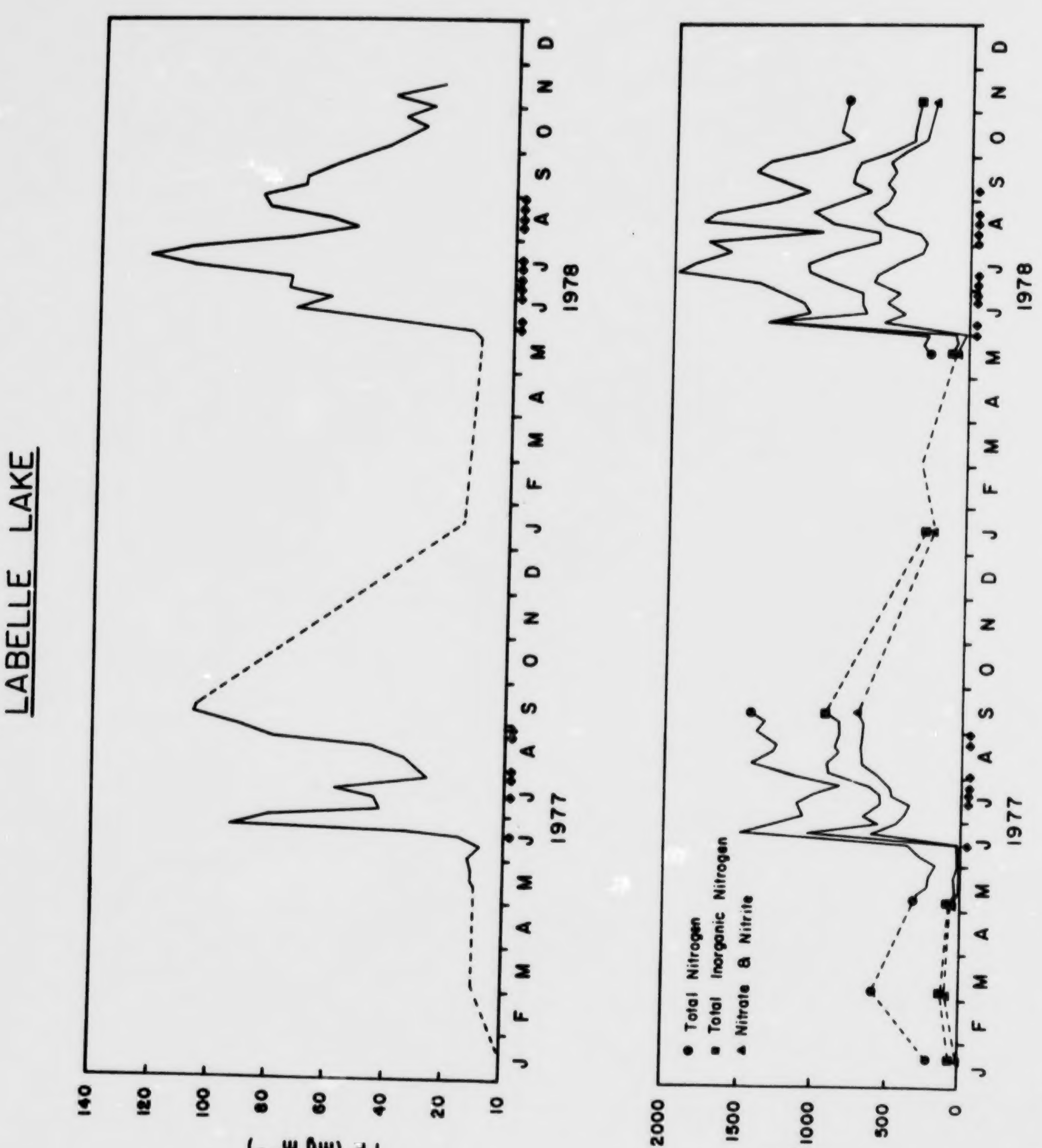


Fig.7-22



LABELLE LAKE

Fig.7-23

MOUNTAINTOP LAKE

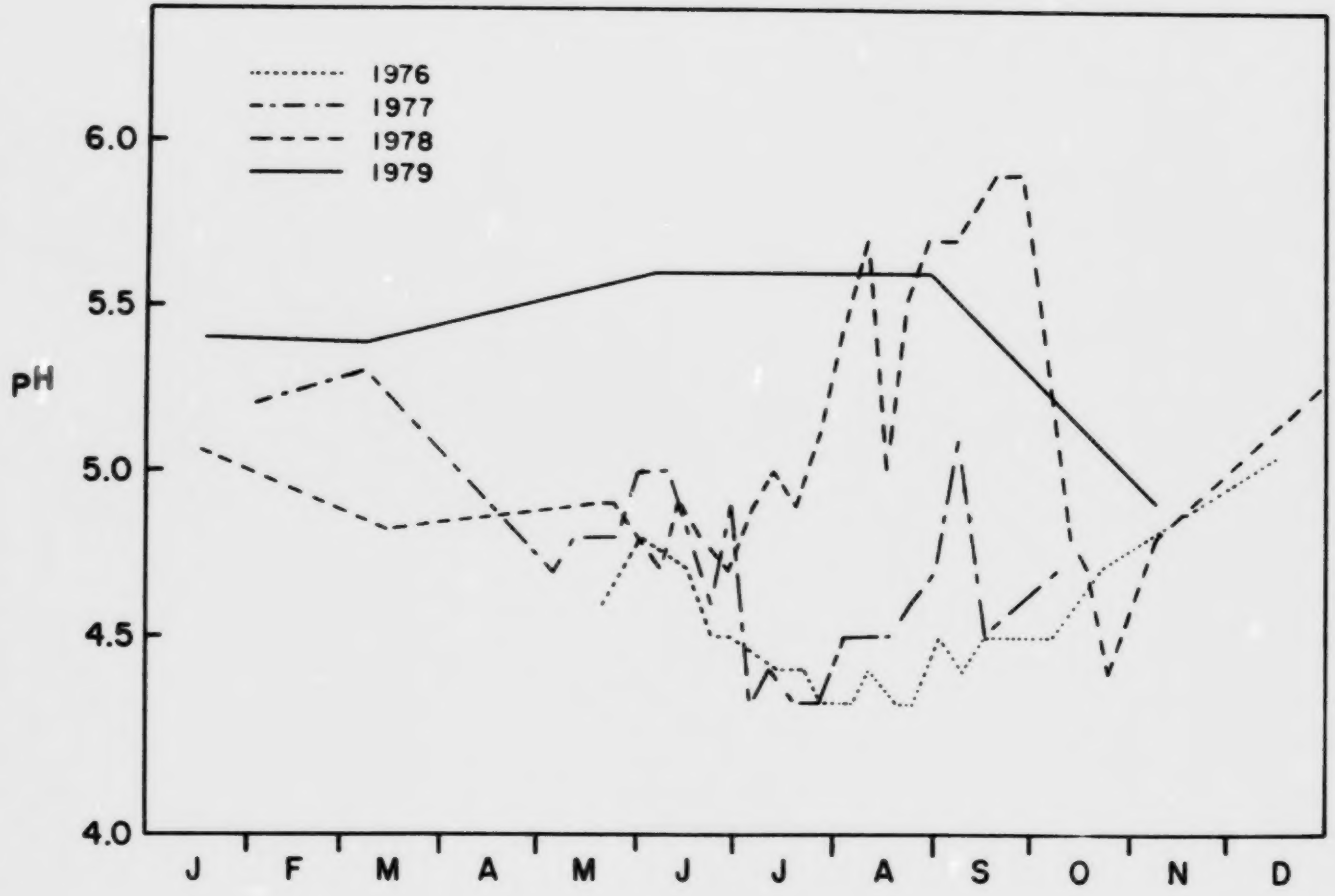


Fig.7-24

MOUNTAINTOP LAKE - Isopleths of pH

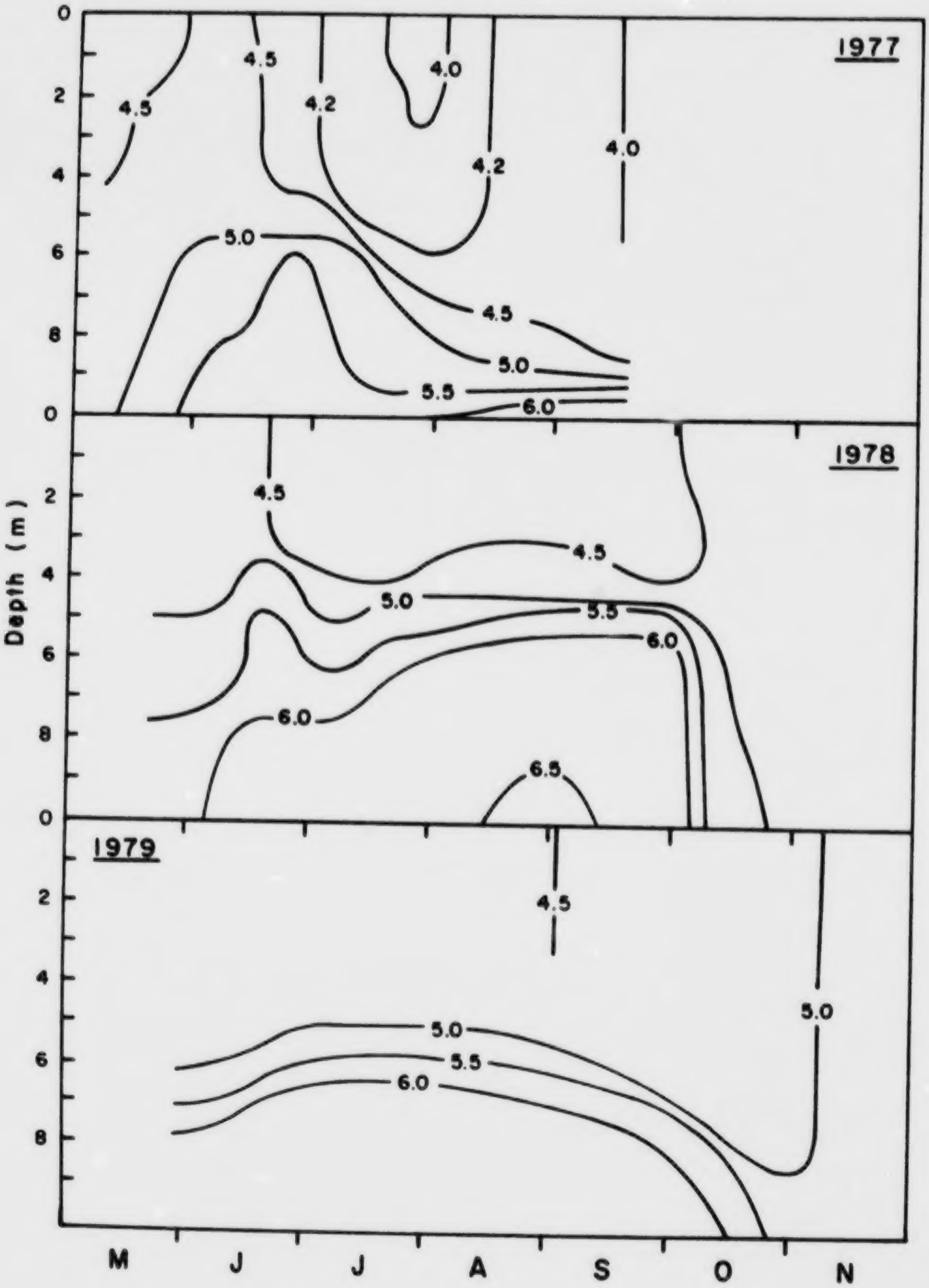


Fig.7-25

Vertical DIC profiles (mg L^{-1} of C) in Mountaintop Lake.

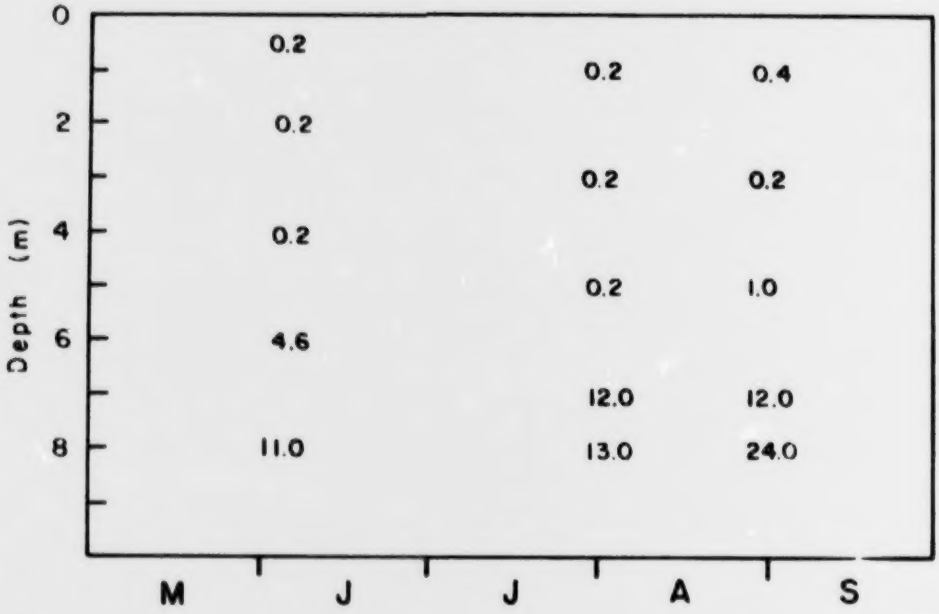


Fig.7-26

MOUNTAINTOP LAKE

Alkalinity isopleths (mg $L^{-1} CaCO_3$)

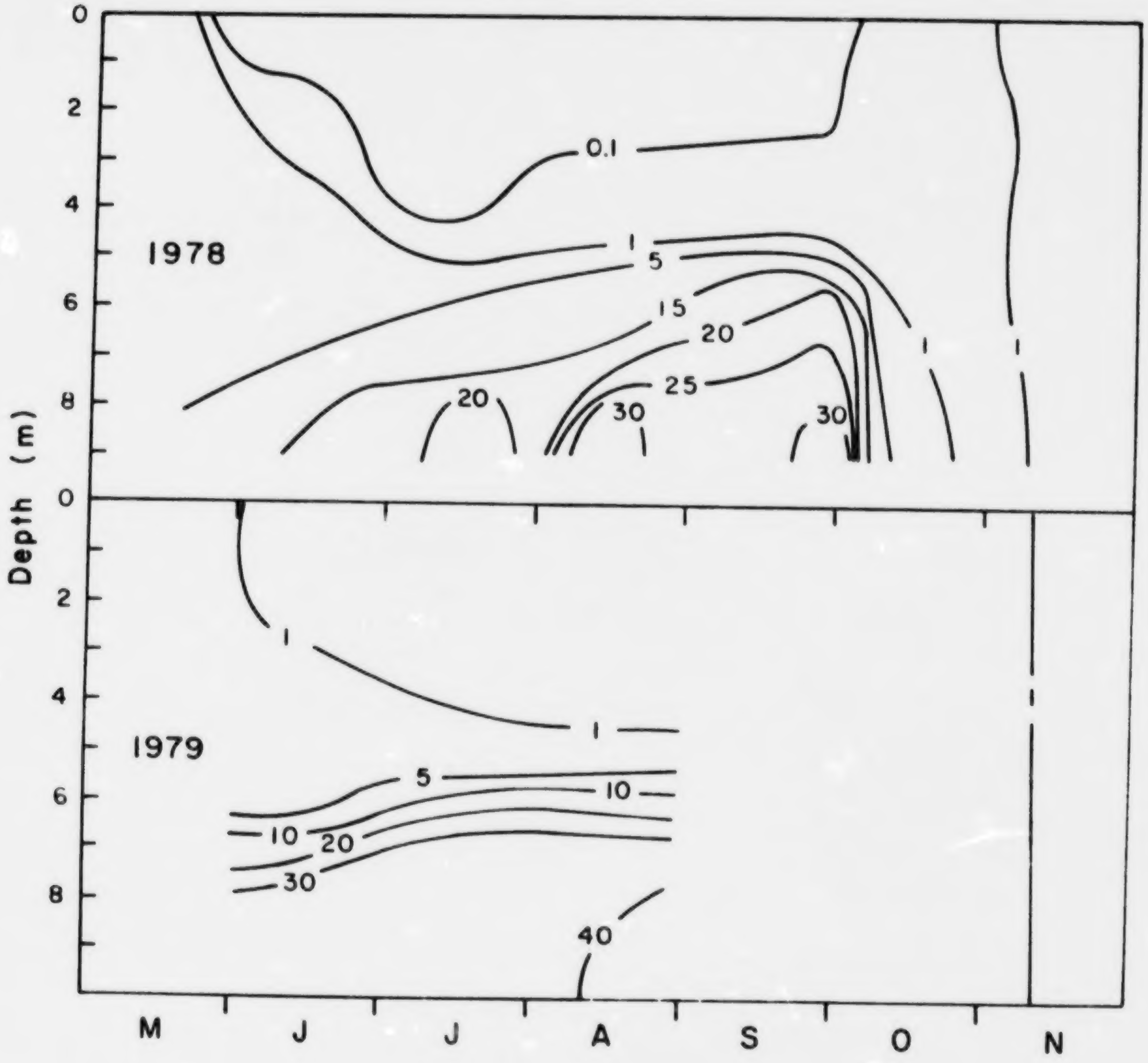


Fig.7-27

LABELLE LAKE

pH Isopleths

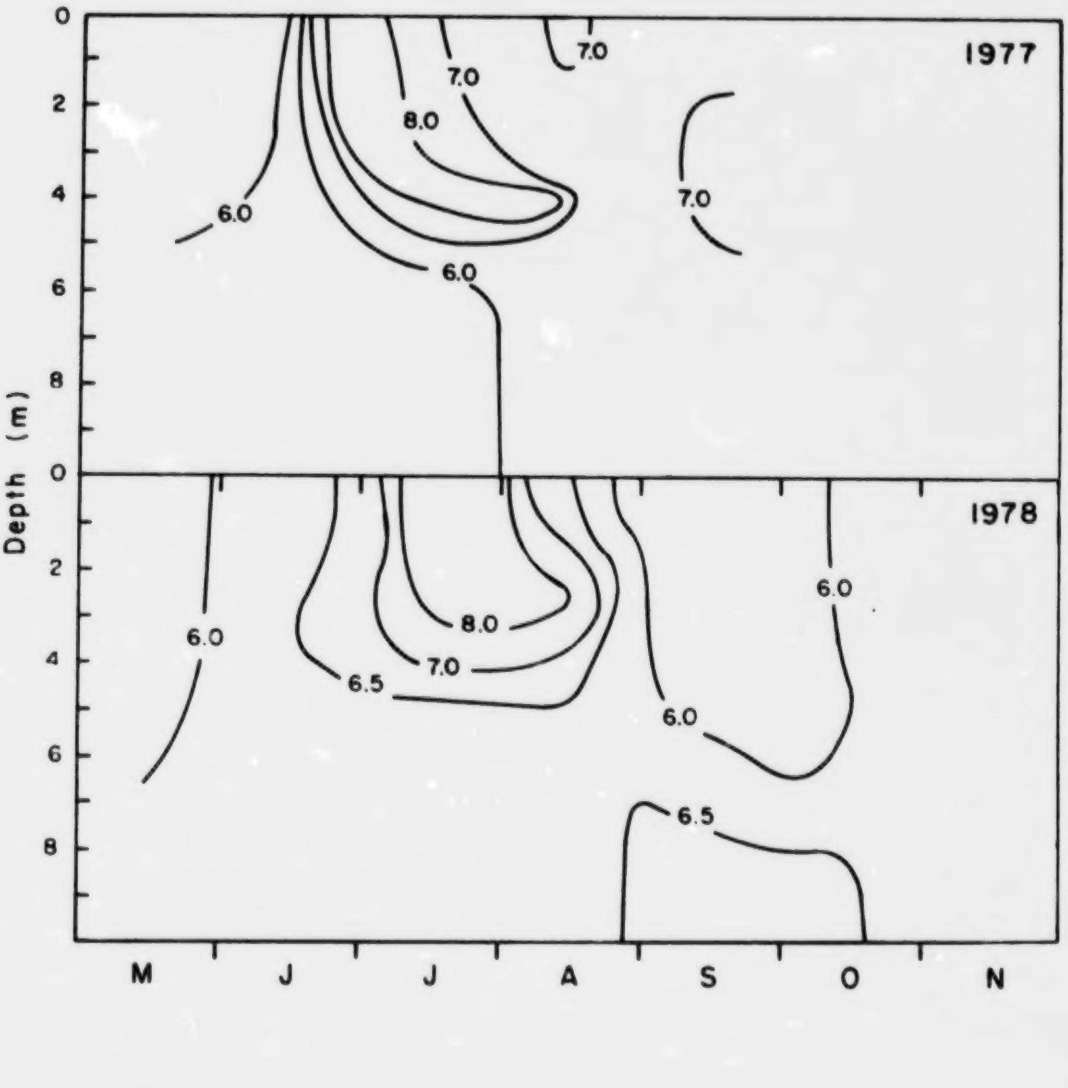


Fig.7-28

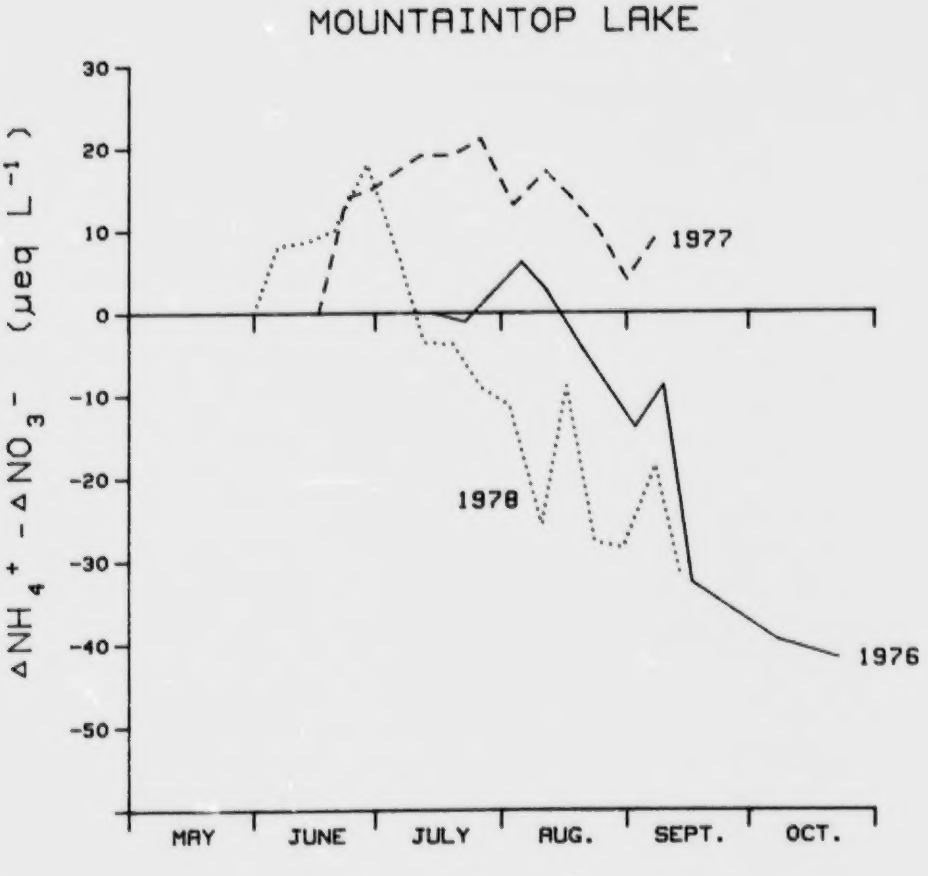

MOUNTAINTOP LAKE
30
20
10
0
-10
-20
-30
-40
-50
$\Delta NH_4^+ - \Delta NO_3^-$ (µeq L^{-1})
1977
1978
1976
MAY
JUNE
JULY
AUG.
SEPT.
OCT.

Fig.7-29

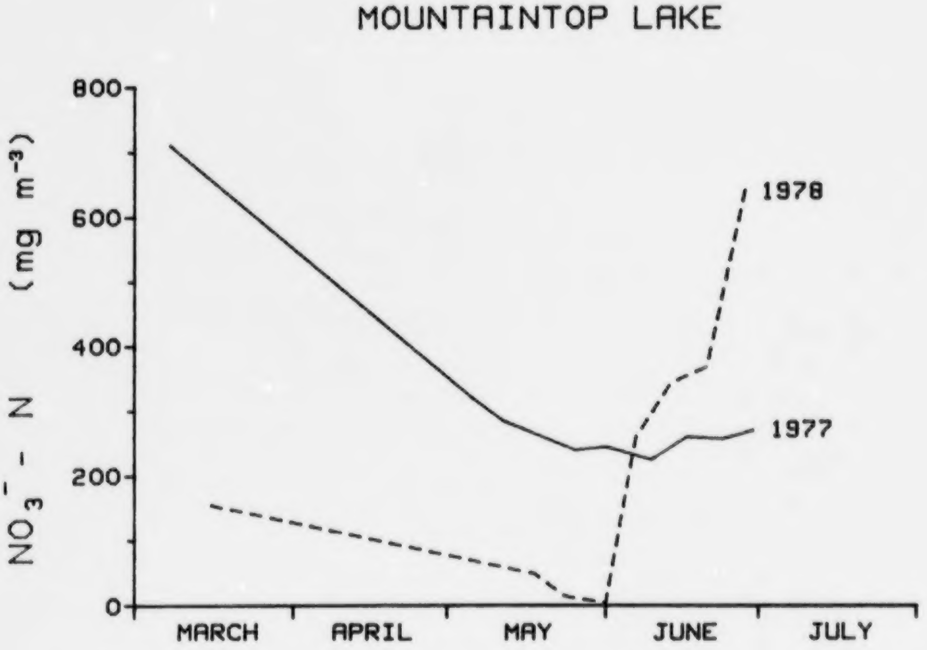

MOUNTAINTOP LAKE
$NO_3^- - N$ (mg m^{-3})
800
600
400
200
0
MARCH
APRIL
MAY
JUNE
JULY
1978
1977

Fig.7-30

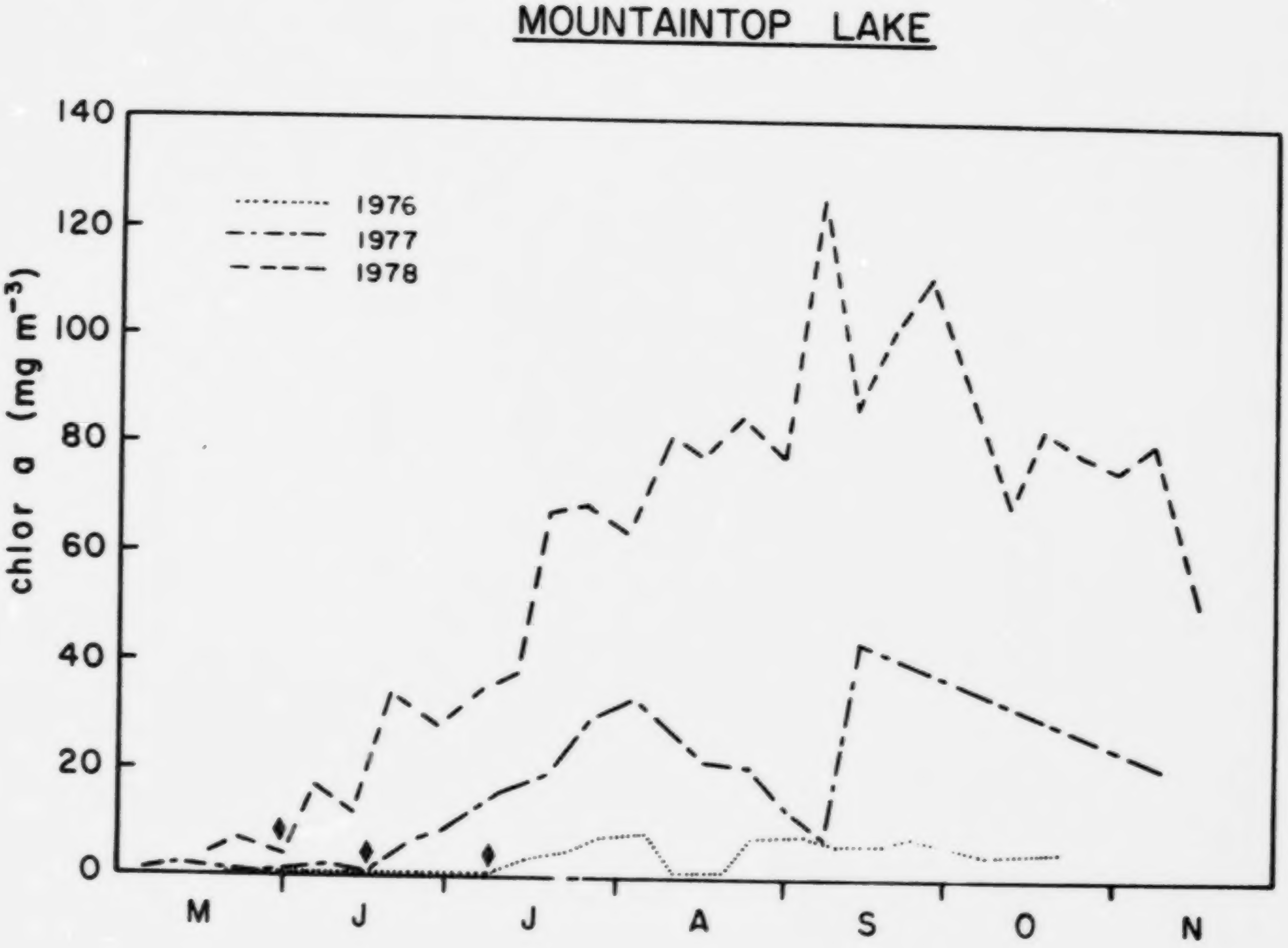

MOUNTAINTOP LAKE
chlor a (mg m^{-3})
140
120
100
80
60
40
20
0
1976
1977
1978
M
J
J
A
S
O
N

Fig.7-31

MOUNTAINTOP LAKE

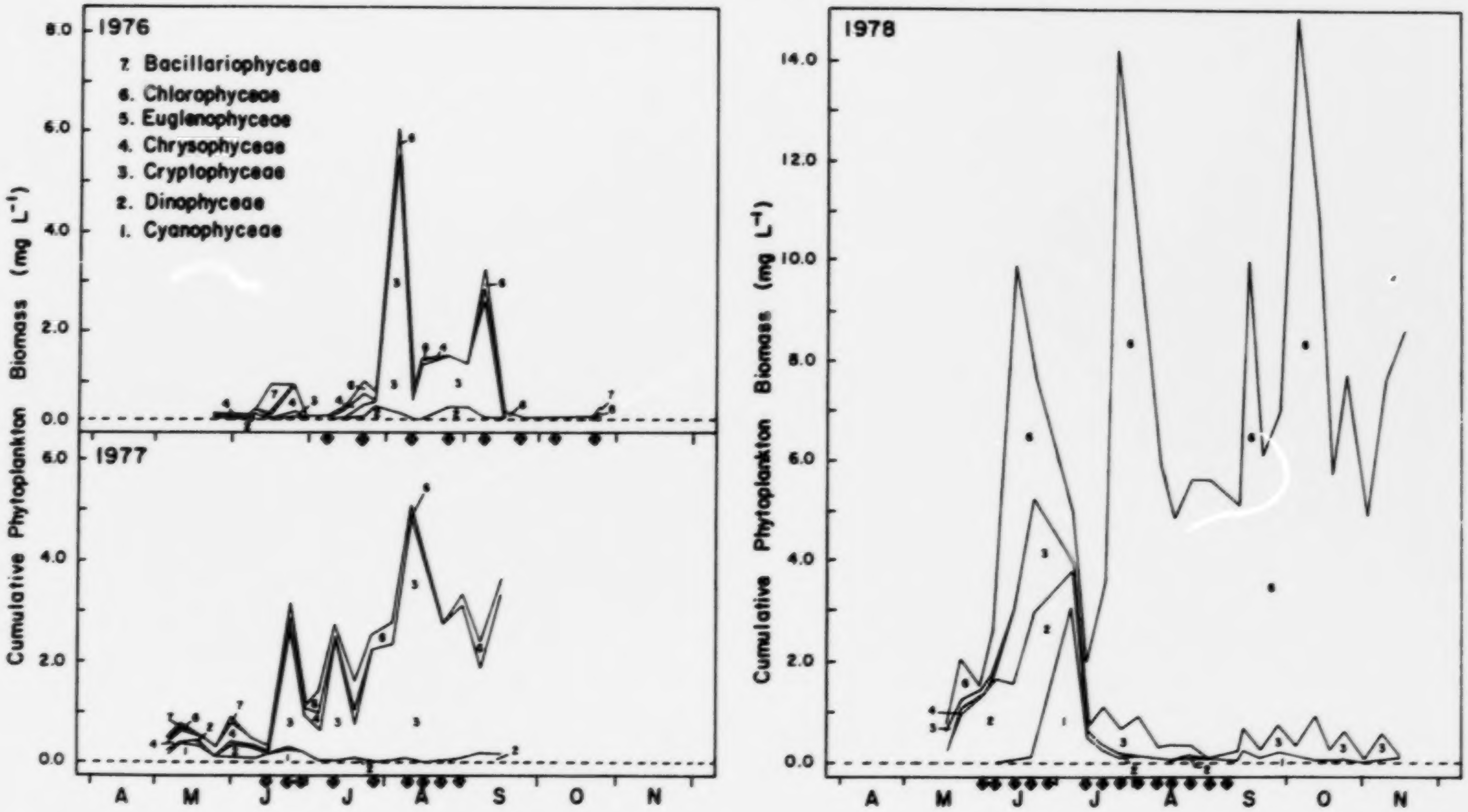


Fig.7-32

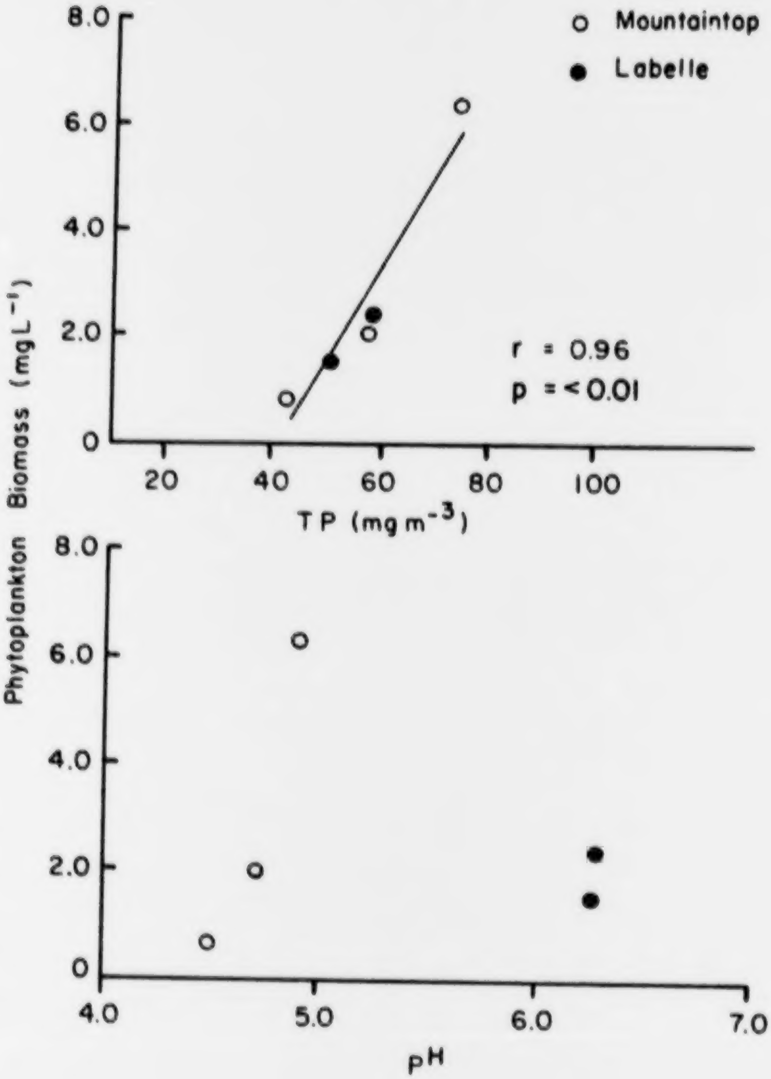

○ Mountaintop
● Labelle
r = 0.96
p = <0.01
Phytoplankton Biomass (mgL⁻¹)
8.0
6.0
4.0
2.0
0
20
40
60
80
100
TP (mg m⁻³)
4.0
5.0
6.0
7.0
pH

Fig.7-33

MOUNTAINTOP LAKE

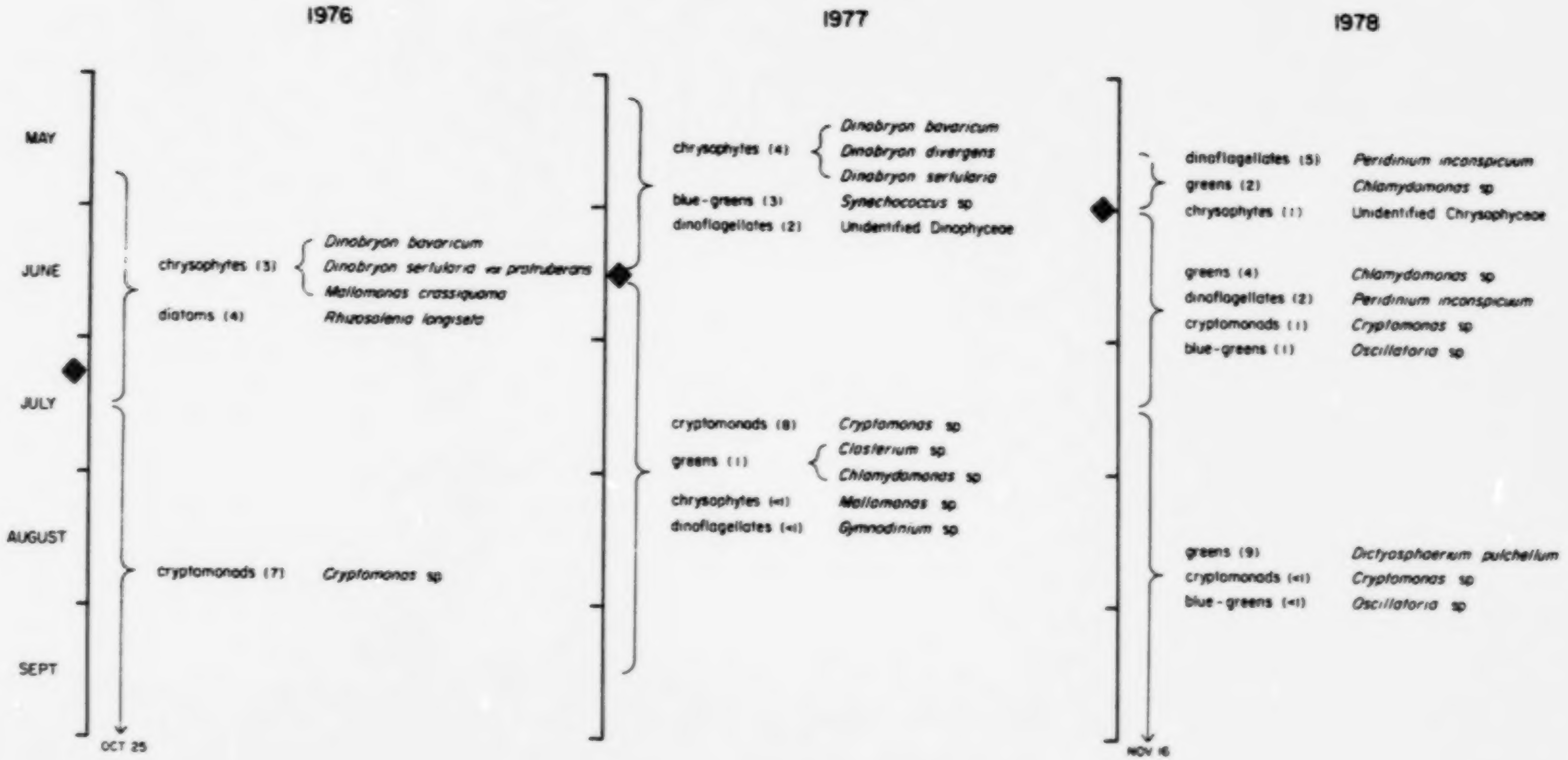
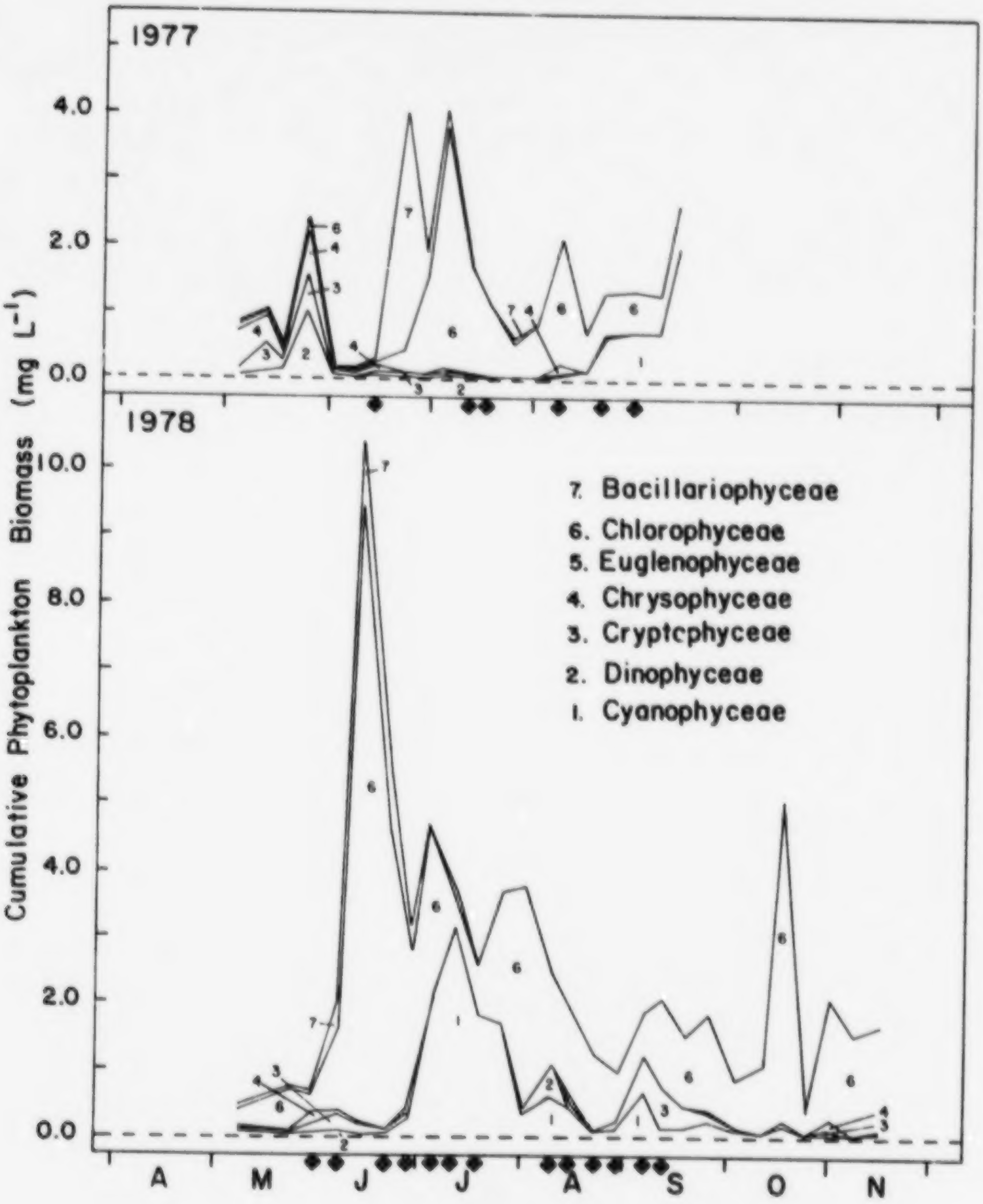


Fig.7-34



LAKE LABELLE

Fig.7-35

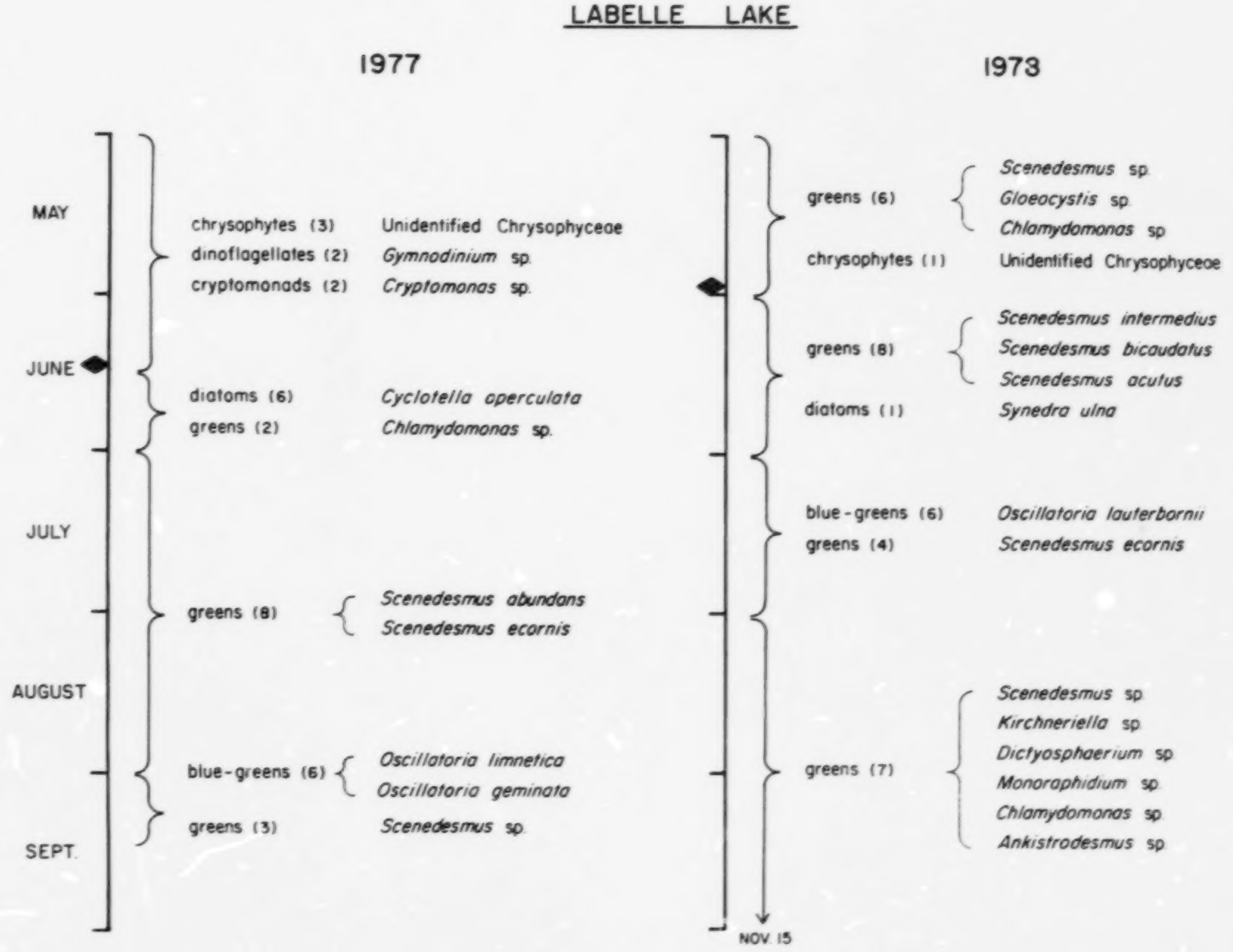
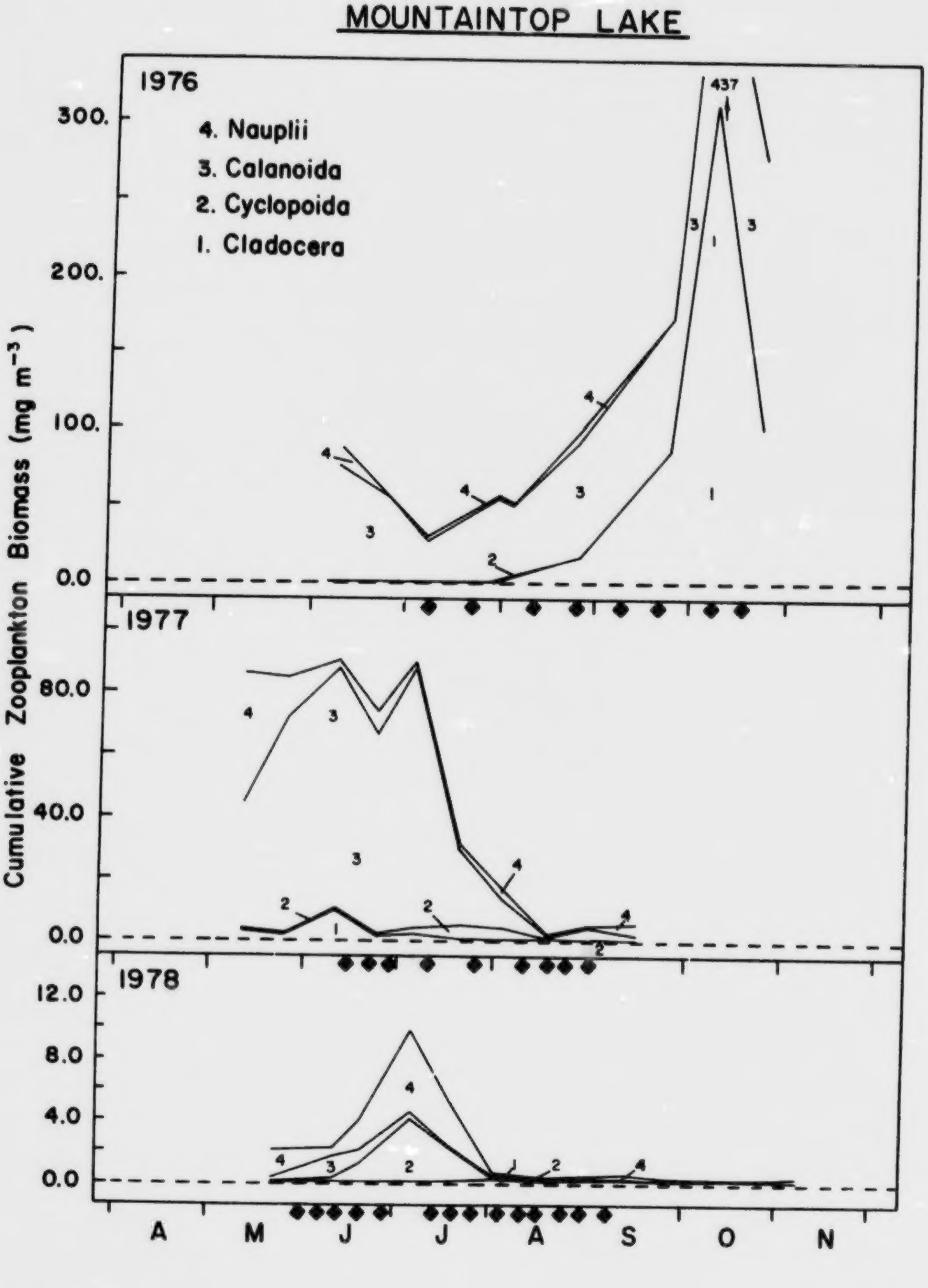

LABELLE LAKE
1977
1973
MAY
JUNE
JULY
AUGUST
SEPT.
chrysophytes (3) Unidentified Chrysophyceae
dinoflagellates (2) Gymnodinium sp.
cryptomonads (2) Cryptomonas sp.
diatoms (6) Cyclotella operculata
greens (2) Chlamydomonas sp.
greens (8) Scenedesmus abundans, Scenedesmus ecornis
blue-greens (6) Oscillatoria limnetica, Oscillatoria geminata
greens (3) Scenedesmus sp.
greens (6) Scenedesmus sp., Gloeocystis sp., Chlamydomonas sp
chrysophytes (1) Unidentified Chrysophyceae
greens (8) Scenedesmus intermedius, Scenedesmus bicaudatus, Scenedesmus acutus
diatoms (1) Synedra ulna
blue-greens (6) Oscillatoria lauterbornii
greens (4) Scenedesmus ecornis
greens (7) Scenedesmus sp, Kirchneriella sp, Dictyosphaerium sp, Monoraphidium sp, Chlamydomonas sp, Ankistrodesmus sp
NOV. 15

Fig.7-36



MOUNTAINTOP LAKE
1976
4. Nauplii
3. Calanoida
2. Cyclopoida
1. Cladocera
437
300.
200.
100.
0.0
1977
80.0
40.0
0.0
1978
12.0
8.0
4.0
0.0
Cumulative Zooplankton Biomass (mg m^{-3})
A
M
J
J
A
S
O
N

Fig.7-37

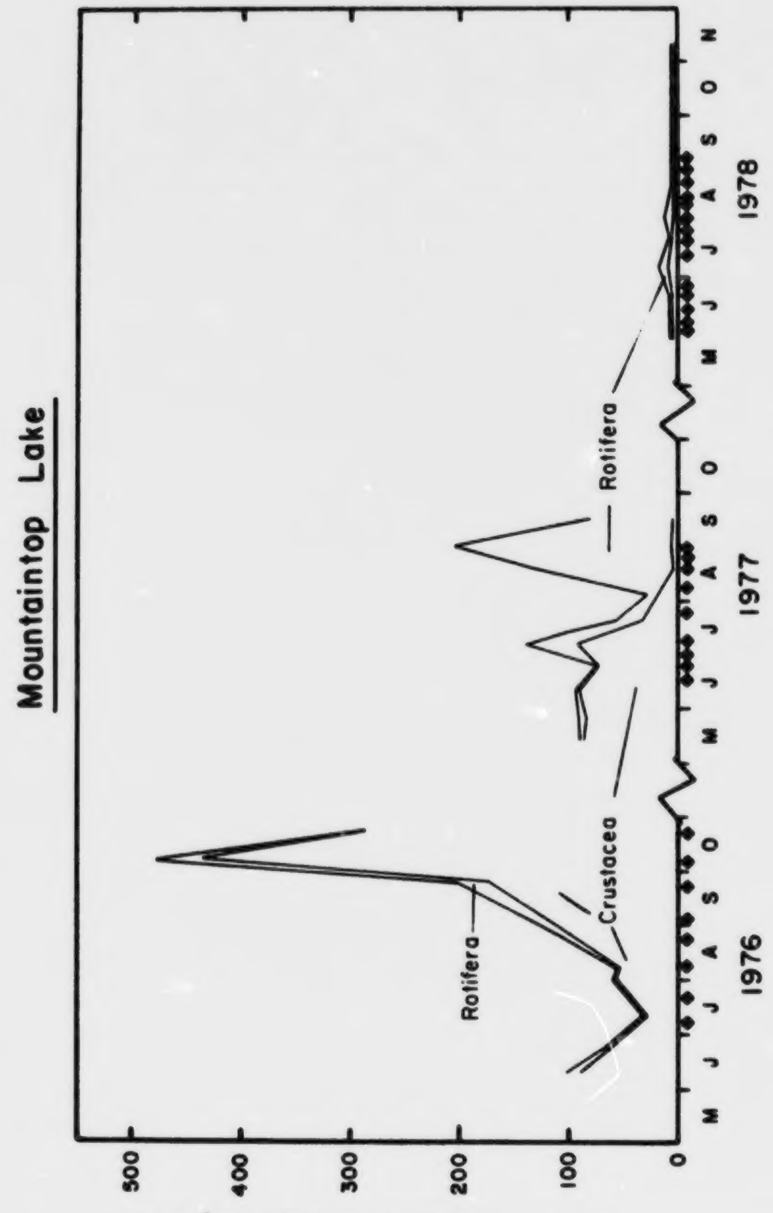

Mountaintop Lake
Cumulative Zooplankton Biomass (mg m⁻³)
0
100
200
300
400
500
Rotifera
Crustacea
Rotifera
M
J
J
A
S
O
N
1976
1977
1978

Fig.7-38

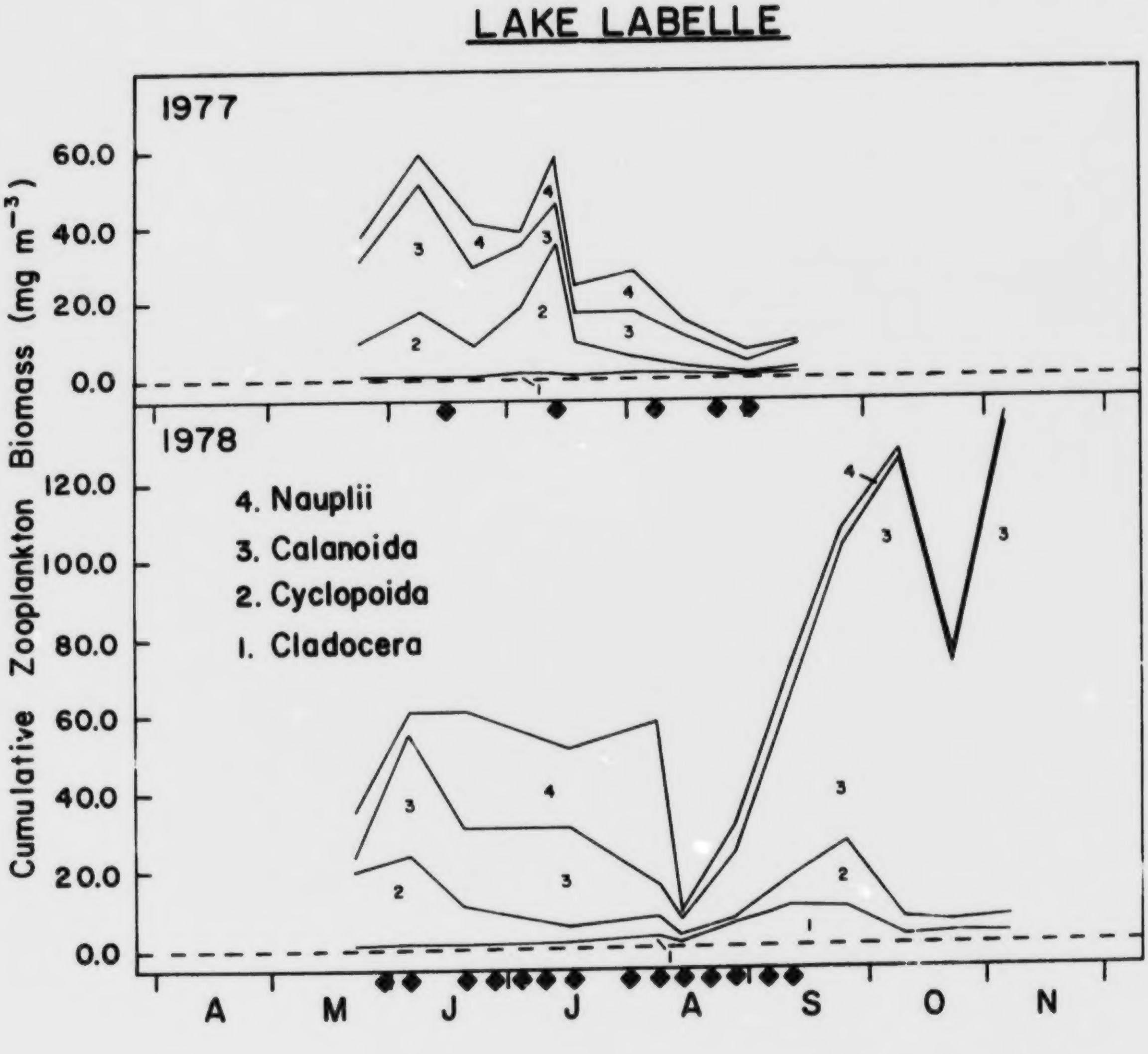

LAKE LABELLE
1977
1978
Cumulative Zooplankton Biomass (mg m⁻³)
60.0
40.0
20.0
0.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
4. Nauplii
3. Calanoida
2. Cyclopoida
1. Cladocera
4
3
2
1
A
M
J
J
A
S
O
N

Fig.7-39

LABELLE LAKE

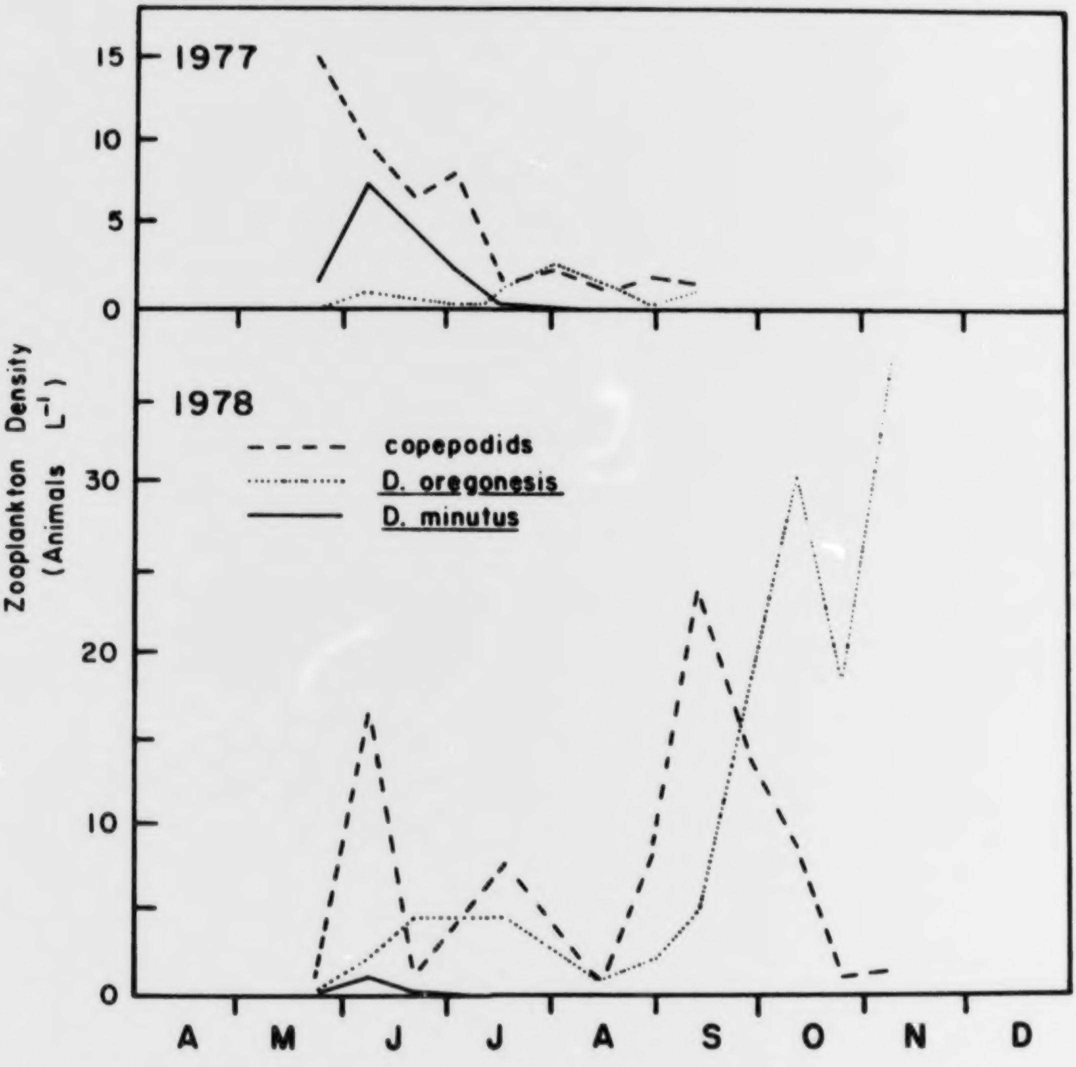


Fig.7-40

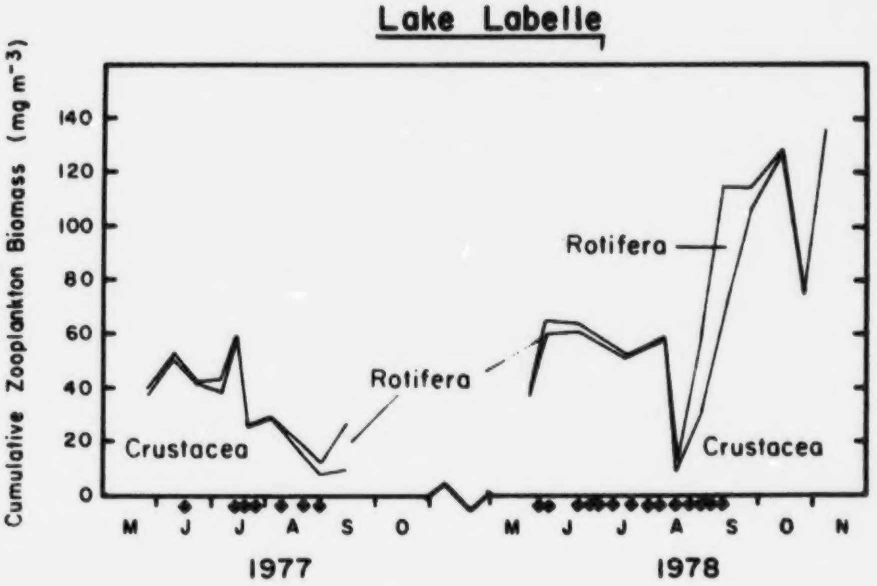
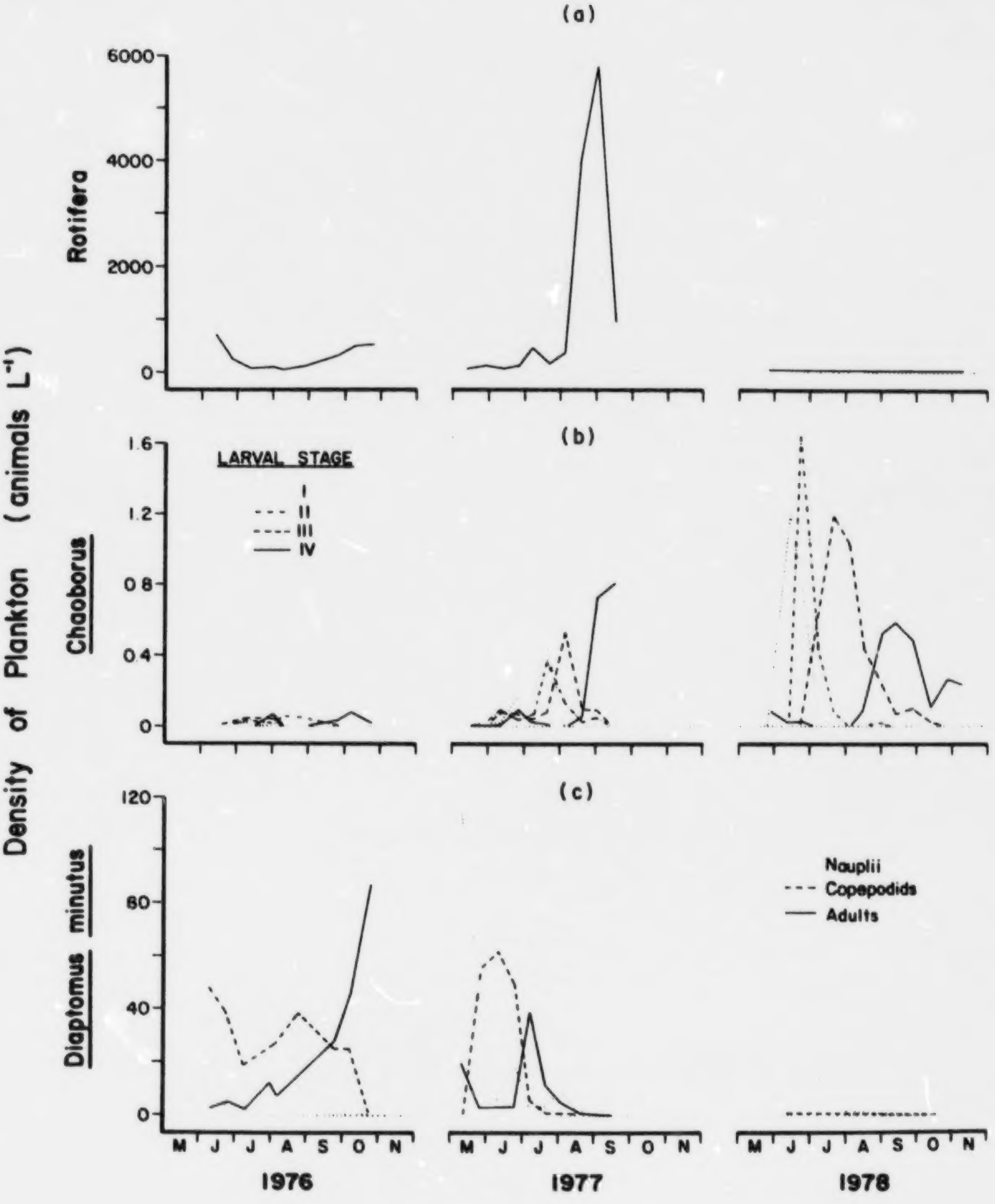

Lake Labelle
Cumulative Zooplankton Biomass (mg m⁻³)
140
120
100
80
60
40
20
0
Rotifera
Rotifera
Crustacea
Crustacea
M
J
J
A
S
O
M
J
J
A
S
O
N
1977
1978

Fig.7-41


(a)
(b)
(c)
Density of Plankton (animals L⁻¹)
Rotifera
6000
4000
2000
0
Chaoborus
1.6
1.2
0.8
0.4
0
LARVAL STAGE
I
II
III
IV
Diaptomus minutus
120
80
40
0
Nauplii
Copepodids
Adults
M J J A S O N
1976
1977
1978

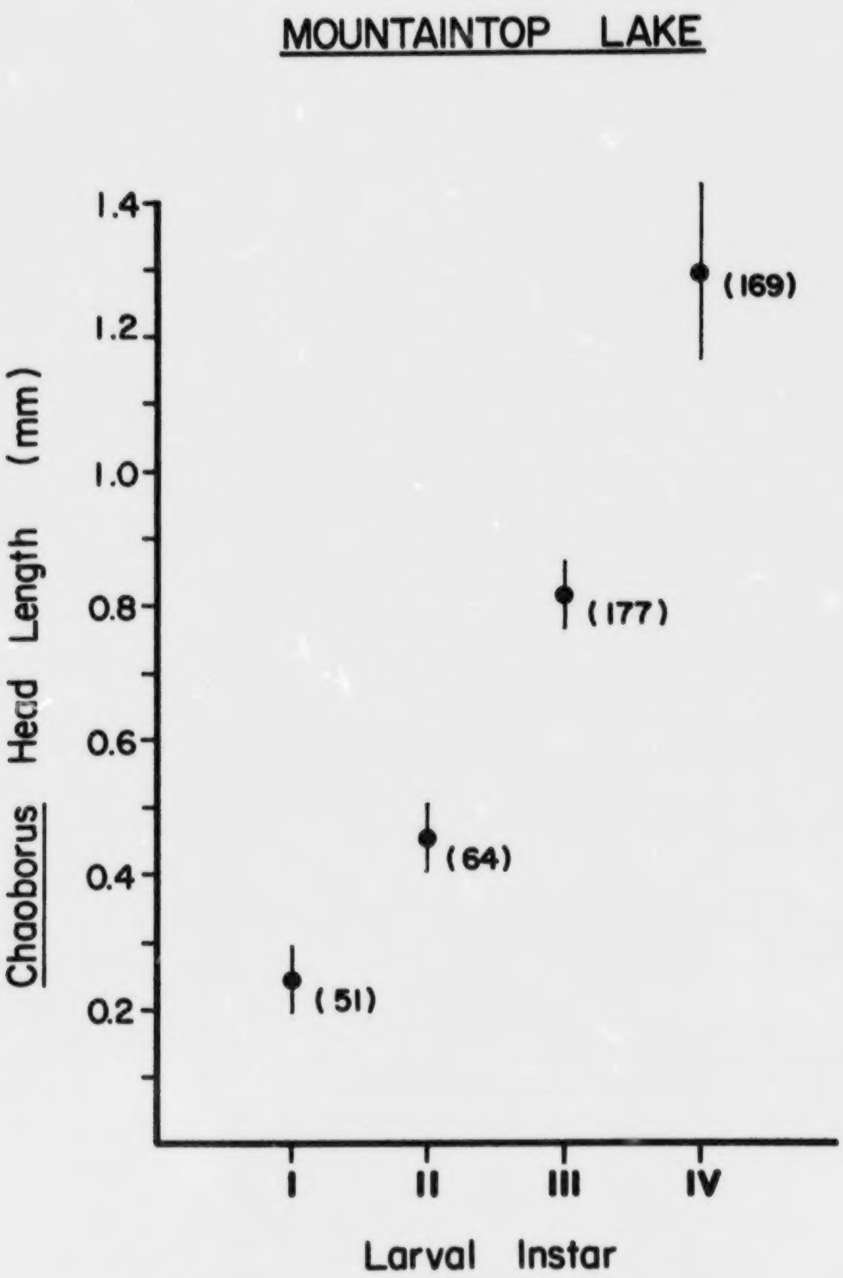

MOUNTAINTOP LAKE
Chaoborus Head Length (mm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
(169)
(177)
(64)
(51)
I
II
III
IV
Larval Instar

Fig.7-43

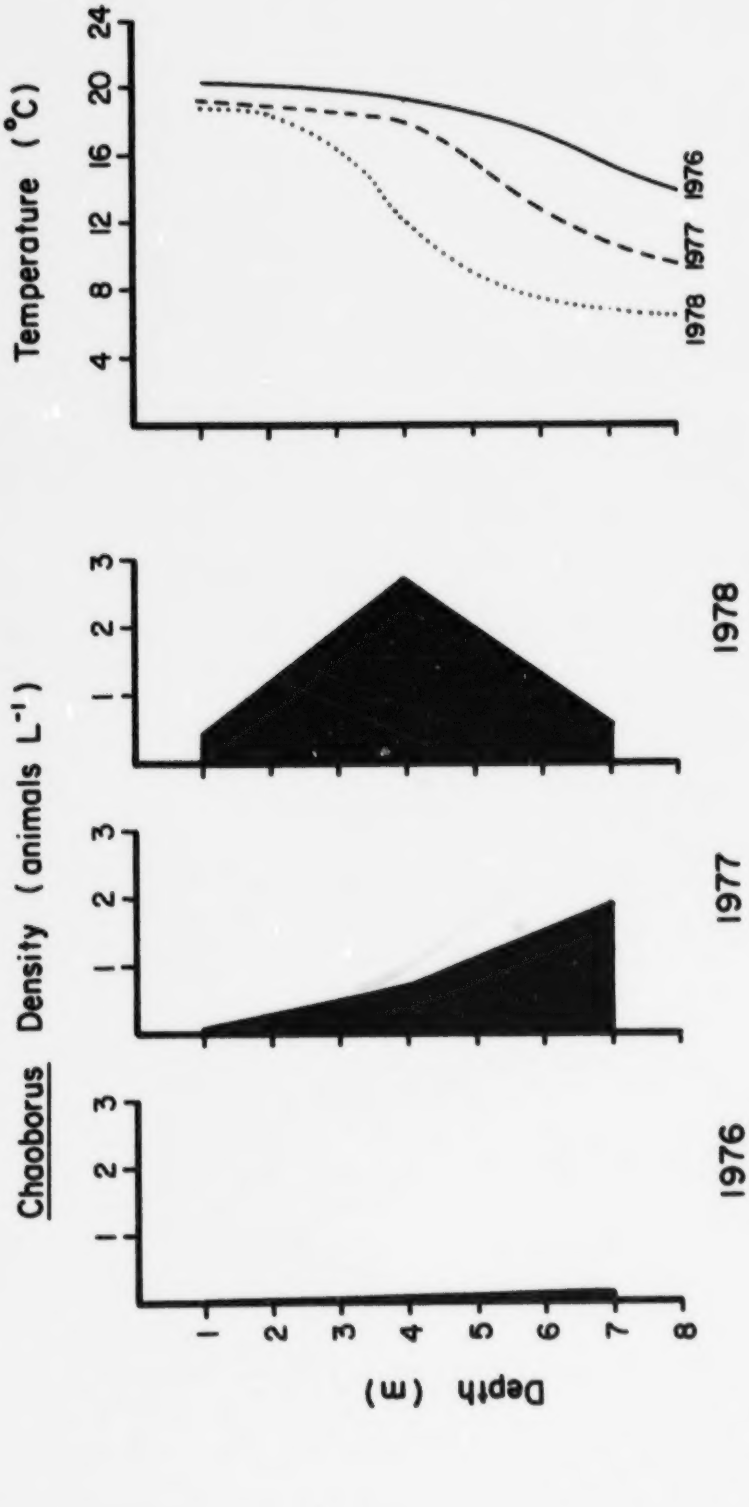
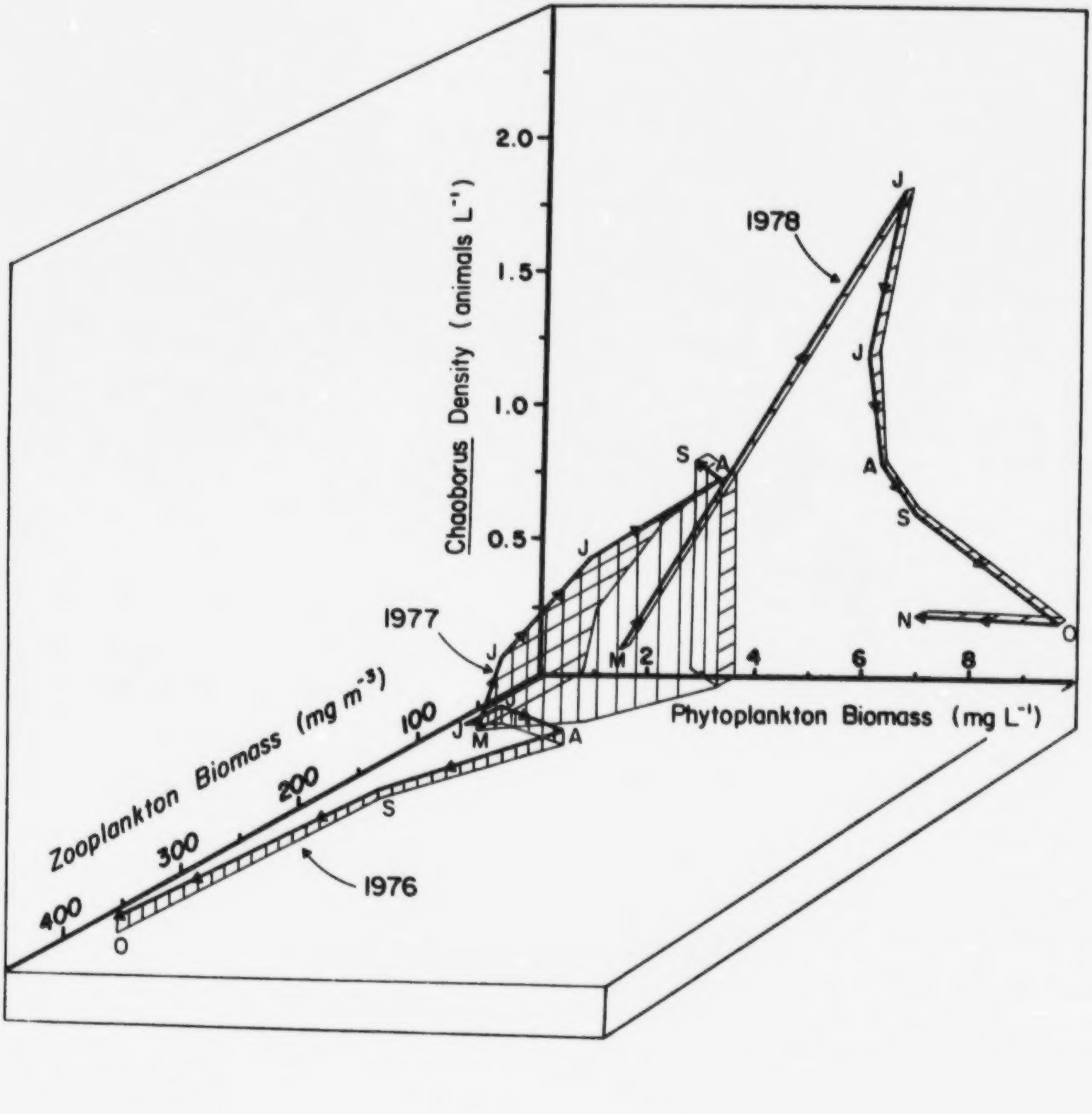

Temperature (°C)
24
20
16
12
8
4
1976
1977
1978
Chaoborus Density (animals L⁻¹)
3
2
1
1978
1977
1976
Depth (m)
1
2
3
4
5
6
7
8

Fig.7-44



Chaoborus Density (animals L⁻¹)
2.0
1.5
1.0
0.5
Phytoplankton Biomass (mg L⁻¹)
2
4
6
8
Zooplankton Biomass (mg m⁻³)
100
200
300
400
1978
1977
1976
J
J
A
S
N
O
S
A
J
J
M
J
M
A
S
O

CHAPTER 8

MASS BALANCE MODELS: AN EXPLANATION OF THE OBSERVED CHEMISTRY OF LAKES NEAR SUDBURY, ONTARIO

P.J. Dillon

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A. Introduction

A mass balance (or a material budget) of a substance for a lake is simply an accounting of the magnitude of the fluxes of the substance into and out of the lake. For some substances, changes in speciation must also be considered as losses or inputs; for example the reduction of SO_4^{2-} to S^{2-}, if it occurs, must be considered in a SO_4^{2-} mass balance. The sediments of a lake can be a sink (a pool or "compartment" into which material is lost) for some substances and a source for other substances, in which case these fluxes must be included in the mass balance. Once a complete mass balance is obtained, the relative importance of the different sources and of the different loss mechanisms can be assessed.

The measured mass balance of a substance can also be used, with the aid of mathematical models, to predict the concentration of the substance in the lake (Scheider et al. 1979c). These mass balance models are simply mathematical expressions of the law of conservation of mass. In addition to the measured fluxes of the substance, the information required for most mass balance models includes the hydraulic budget and the physical characteristics of the lake (mean depth, area, volume).

Because eutrophication has been a major problem in many parts of the world for at least two decades, most of the limnological mass balance models developed and tested to date have been related to the algal nutrients, particularly phosphorus (Vollenweider 1969, Dillon 1974, Schindler et al. 1978, Oglesby 1977, Reckhow 1979, and Chapra and Robertson 1977). However, many of the principles employed in these models can be applied to other substances.

In this chapter, the hydraulic budgets (Chapter 4), the inputs of materials by bulk deposition (Chapter 2), and the material budgets for the watersheds (Chapter 5) of the study lakes are combined and utilized with a mass balance model to test several hypotheses. These hypotheses include:

a) the concentrations of major ions (Mg^{2+}, Na^+, K^+, and Cl^-) in the study lakes can be predicted accurately from the measured mass balances,

b) the concentrations of Ca^{2+} in the study lakes can be predicted from the measured mass balances and the quantities of neutralizing agents added,

c) the SO_4^{2-} concentrations in the study lakes are greater than predicted on the basis of the measured mass balances because the measured inputs from the atmosphere are underestimates (see Chapters 2, 5),

d) the alkalinity and H^+ mass balances of Clearwater and Lohi Lakes can be used to predict the lakes' pH's and the re-acidification rate of Lohi Lake,

e) the alkalinity and H^+ concentrations of Middle and Hannah Lakes can be predicted on the basis of the measured mass balances prior to, but not following, fertilization treatments,

f) the biological utilization of NO_3^- and NH_4^+, particularly in the fertilized lakes, plays an important role in these lakes' acid-base balances.

B. Model Development

i. Background

The simplest mass balance models are those developed for substances whose only loss mechanism from the water column of a lake is via outflow. Such substances are termed "conservative". In these cases, sedimentation resulting from chemical or biological processes and loss by gas evolution either do not occur, or more likely, are negligible relative to loss via outflow. Some Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and S, for example, is found in lake sediments, but the quantity sedimented each year is only a small fraction of that passing through the lake (Dillon, unpub. studies). For these substances, chemical transformations are also usually unimportant, the exception being SO_4^{2-}, which may be reduced by microbially-mediated reactions. Elements such as Ca^{2+} may be removed from the water by mineral formation, but at concentrations normally measured in Precambrian lakes, this is very unlikely.

Many of the earliest mass balance models were developed for conservative substances (Biffi 1963, Rainey 1967, Sweers 1969, Dingman and Johnson 1971, O'Connor and Mueller 1970 (summarized by Dillon 1974)). Biffi (1963), Rainey (1967) and Dingman and Johnson (1971) treated lakes as mixed reactors with constant input rates, while Sweers (1969) used multi-layer models to account for thermal stratification of lakes. O'Connor and Mueller (1970) considered cases in which the input rates were not constant, but altered in several specified ways. The models developed by Sweers (1969) and O'Connor and Mueller (1970) demonstrated good predictive capabilities for Cl^{-} concentrations in the Great Lakes. No tests of any of these models to determine their predictive capability for other substances have been reported.

Subsequent mass balance model development has emphasized phosphorus (Vollenweider 1969, 1975, 1976, Reckhow 1979, Dillon and Rigler 1975, and Imboden 1974). Increasing complexities such as spatial (vertical, horizontal) heterogeneity and short-term temporal variability have been included. Some concepts from several of these models have been utilized in the following model development. However, with the exception of Nelson Lake, the study lakes are small, with a single basin and a small (if any) hypolimnetic volume relative to the whole-lake volume, indicating that relatively simple models should be adequate for predicting lake chemistry.

ii. Development of Model

If, (a) the input rate of a substance, X, to a lake is constant,

(b) the input is instantly and uniformly mixed throughout the water body (ie. the lake is treated as a continuously stirred tank reactor - CSTR), and

(c) the material is lost from the lake only by outflow and does not undergo chemical or biological transformations in the water body,

then, the rate of change of the concentration of X in the water is defined by:

$$\frac{d[X]}{dt} = \frac{J}{V} - \frac{Q}{V} [X]_o \qquad (8\text{-}1)$$

where

J	is the constant total input per unit time
V	is the lake volume
Q	is the constant discharge from the lake's outflow per unit time
$[X]_0$	is the concentration of X in the outflow

If it is assumed that the outflow concentration is equal to the lake concentration ($[X] = [X]_0$), then equation 8-2 defines the concentration of X as a function of time:

$$[X]_t = \exp(-Qt/V)\,[X]_i + J\,(1 - \exp(Qt/V))/Q \qquad (8\text{-}2)$$

where $[X]_t$ = concentration at time t

$[X]_i$ = initial concentration

The steady-state concentration, that is, the concentration which is asymptotically approached (ie. as $t \rightarrow \infty$) is defined as

$$[X]_{ss} = J/Q \tag{8-3}$$

If the input rate is changed from one constant level, J_1, to a new level, J_2, the time required for the concentration to increase (or decrease) from the original steady-state level halfway to a new steady-state level is given by:

$$t_{1/2} = \frac{V}{Q} \ln 2$$

$$\text{or } t_{1/2} = \frac{\ln 2}{\rho} \tag{8-4}$$

where the flushing rate $\rho = Q/V$.

For 90% change (3.3 half-times, referred to as the response time), the time required is $3.3 \ln 2/\rho$ or $2.3/\rho$.

This model can be used as equation 8-3 to determine if the measured input rates are adequate to explain the observed lake concentrations for those substances that are at steady-state levels (ie. those whose concentration has remained constant for an extended time). In cases where the input rates have changed, equation 8-2 can be used if new steady-state concentrations have not been reached. Conversely, input rates required to achieve measured steady-state concentrations or measured changes in concentration over specified time periods can also be calculated from equations 8-2 and 8-3 by solving for J.

C. Mass Balance Calculations

i. Data Sources

In order to utilize the model developed in the previous section to make predictions about the chemical composition of the study lakes, hydrologic budgets and mass balances for the substances of interest are required.

The major inputs of water and of the chemical substances studied to Clearwater, Lohi, Hannah, Middle and Nelson Lakes result from deposition directly on the lakes' surfaces, from runoff from the terrestrial portion of the lakes' watersheds, and from outflow from upstream lakes. The input via runoff from the lakes' watersheds may be either from gauged (or calibrated) watersheds or from the ungauged portion of the terrestrial watersheds. Water balances for the 5 study lakes for the period June 1977 - December 1979 are described in Chapter 4. Inputs of substances to the study lakes throughout the same time period via bulk deposition onto the lakes' surfaces are summarized in Chapter 2, while outputs from the gauged watersheds into the lakes are discussed in Chapter 5. Inputs from the ungauged portions of the lakes' watersheds were calculated by proration (on an areal basis) of inputs from nearby gauged watersheds. These extrapolations from gauged to ungauged areas should be accurate for Clearwater and Nelson Lakes, each of which had several gauged tributaries, and for Lohi Lake, whose ungauged watershed budgets could be extrapolated from the nearby Clearwater Lake tributaries. However, there were no gauged tributaries to Hannah or Middle Lakes. Mass balances for the Middle Lake inflow 1 watershed were not based on measured hydrology (Chapter 5). Because these data are less precise, data from the Clearwater Lake tributaries were also used. This subject is discussed in subsequent sections of this chapter.

There has also been evidence presented that the input of at least SO_4^{2-} and H^+ by atmospheric deposition to the watersheds has been underestimated because of the addition of unmeasured contributions as dry fallout (Chapters 2, 5). This same underestimate may be incorporated in the measurement of the input directly to the study lakes' surfaces. This is also discussed more fully in subsequent sections.

Mass balances for each of the study lakes for Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, H^+, TIA (total inflection-point alkalinity), TP, NO_3^-, NH_4^+, TKN, Al, Mn, Fe, Cu, Ni and Zn are summarized in Appendix 10 for the June 1977 - December 1979 period. No material or water budgets were measured prior to this time. Therefore, any attempts to use the mass balance model to make predictions between June 1973 (the beginning of the study) and May 1977 (ie. prior to measurement of budgets) must necessarily be less precise than later attempts made using measured data. For this earlier period, estimates of the material budgets were made, either by assuming the measured data for the later period are also representative of this earlier period, or by estimating the earlier inputs from the lakes' chemistry (ie. by reversing the usual modelling procedure). In the case of the water balance, long-term climatological and hydrological information was used to approximate the long-term water balance (Chapter 4, Appendix 3).

ii. Effects of Shutdown of Inco Ltd.

In most of the calculations in this section, the unit of time considered is 1 year, although the monthly mass balances are employed with equation 8-2 to make predictions of short-term variation (monthly or seasonally) in lake chemistry for comparison with measured trends. The first 12-month period, June 1977 to May 1978, precedes the shutdown of the Inco Ltd. smelters, while the second period, June 1978 to May 1979, includes about 8 months during which the Inco Ltd. smelter was shutdown, plus 4 months during which emissions were substantially lower than the average of the previous years. If the mass balance data are divided into annual budgets on a calendar year basis, then both complete years include some portion of the shutdown time period, a situation that is less desirable.

The response times of the study lakes (Table 8-1) are long relative to the length of the shutdown. Therefore, only very large changes in input over this 8-month period could have resulted in measurable effects on the study lakes' chemistry. Even moderate changes in input may not have resulted in measurable changes in lake chemistry. For example, a 50% reduction in the input rate of a substance to Clearwater Lake would have resulted in a change in lake concentration of <15% after 8 months. The measurable effects of shutdown on lake chemistry would be further reduced if there was a delayed washout of substances from the watersheds (discussed in Chapter 5). However, any reduction in inputs to the lakes during this period would, if incorporated into the modelling, affect both the long-term predictions and any attempts to validate or calibrate the model by comparison with lake concentrations measured prior to the collection of the mass balance data.

Because the input of any substance to a lake is a function of the lake's water budget, a direct comparison of the loads before and after the smelter shutdown cannot be made. The measured hydraulic discharge to all study lakes was greater in the second 12-month period (June 1978 - May 1979) than in the first (June 1977 - May 1978), the increases ranging from 12 to 72%. This increase

Table 8-1. Response time (3.3 $t_{1/2}$ - equation 8-4) of the study lakes (yr).

Lake	Response time
Clearwater	8.4
Lohi	2.4
Hannah	5.8
Middle	3.2
Nelson	13.4

alone might offset any reduction in concentration of the substances in the lakes' inflows or in bulk deposition resulting from the smelter shutdown.

To ascertain the possible effects of shutdown on the lakes' material budgets, the inputs for the period October 1978 - May 1979 (during shutdown) were compared to those of the previous same 8 months (October 1977 - May 1978). The statistical method used was identical to that employed for the evaluation of the effects of shutdown on bulk deposition (Scheider *et al*. in press).

The total monthly input (J) of each substance was divided by the total monthly discharge of water (Q) for each lake. The resultant parameter (J/Q) is equivalent to the volume-weighted mean concentration of all of the inputs to the lake. This comparison does not take into consideration the possibility that the watersheds may respond slowly to a change in deposition.

The results of the statistical comparisons are given in Table 8-2 for the 6 parameters most likely to have been affected by shutdown. The impact of shutdown on the "downstream" lakes (Lohi and Middle) is expected to be much less than that on the other lakes. This arises because a major input to the "downstream" lakes, outflow from the upstream lakes, will be affected very little over an 8-month period because of the storage capacity of the upstream lakes. Furthermore, it has been indicated in Chapters 2 and 5 that the material budgets of some substances, particularly SO_4^{2-} and H^+, are underestimated because of unmeasured inputs of SO_2. Shutdown would be expected to reduce these inputs, since most of the SO_2 must result from local sources, but the change would be missed. The material budgets of the products of the weathering reactions (such as Ca^{2+}) may also be affected. However, these

Table 8-2. Results of test of the hypothesis that the volume-weighted input (J/Q) was greater in the period June 1977 - May 1978 than in June 1978 - May 1979. Numbers reported are p; n.s. = not significantly different.

Lake	Ca^{2+}	SO_4^{2-}	H^+	Cu	Ni	Zn
Clearwater	n.s.	n.s.	n.s.	0.005	n.s.	0.05
Lohi	n.s.	n.s.	n.s.	0.025	n.s.	n.s.
Hannah	n.s.	n.s.	0.05	0.005	0.055	0.025
Middle	n.s.	n.s.	n.s.	0.005	n.s.	n.s.
Nelson	n.s.	n.s.	n.s.	0.005	n.s.	0.05

effects may also be missed, since the Hannah Lake budgets, and in part, Middle Lake budgets, were estimated in part from Clearwater Lake mass balances which are affected less because of distance from the smelters (Chapter 5). Therefore, a statistical comparison of the mass balances before and during shutdown is most realistic for Clearwater and Nelson Lakes and less realistic for Lohi, Middle and Hannah Lakes.

For all 5 lakes, the mean input of Ca^{2+} and SO_4^{2-} were not significantly reduced, while that of H^+ was significantly lower at Hannah Lake only. Inputs of trace metals, on the other hand, were reduced during shutdown. The mean inflow concentration of Cu to all lakes and Zn to all but the downstream lakes was significantly lower during shutdown. In the case of Ni, there was a reduction at only Hannah Lake, the lake for which input directly to the lake's surface was the most important component of the total material budget.

Because of these findings, it appears that the mass balance data for the whole period of collection can be used without consideration of the effects of shutdown except for the trace metals. However, because of the expressed concerns that changes in material budgets would, in some cases, be missed, emphasis is given in the following sections to data collected prior to shutdown.

D. Observed Lake Chemistry

In order to determine whether the steady-state form of the mass balance model is applicable to each lake for each substance, it is necessary to look at the long-term trends in chemical composition of the lakes to see if steady-state has been reached. Summaries of annual average concentration for the major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} and SO_4^{2-}) are given in Tables 8-3 to 8-7, while more detailed chemical data are provided in Appendix 6.

The flushing rates of the study lakes are high enough such that, with the possible exception of Nelson Lake (see Chapter 4), the response times of the lakes (Table 8-1) to a change in input is not long relative to the study period. That is, the 1973-1979 time period is adequate to assess whether there have been changes in the lakes' concentrations over the course of the study.

From these tables it is apparent that, in Clearwater and Lohi Lakes (Table 8-3, 8-4):

a) the Mg^{2+}, Na^{+}, and K^{+} concentrations remained relatively constant from 1973 to 1979, with the exception of a few high values in 1973,

b) the Cl^{-} concentrations increased gradually from 1974 to 1979,

c) the SO_4^{2-} concentrations remained constant from 1974 to 1977, but were higher in 1973 and lower in 1978 and 1979,

d) the Ca^{2+} concentration in Lohi Lake increased after each neutralization treatment, but declined in every year after 1976 (see Chapter 6). The Ca^{2+} concentration in Clearwater Lake appears to have been relatively constant.

In Middle and Hannah Lakes (Tables 8-5, 8-6):

a) the Mg^{2+} and K^{+} concentrations have remained constant from 1973 to 1979,

b) the Cl^{-} and Na^{+} concentrations have increased continuously since 1974,

Table 8-3. Annual average major ion content (mg L^{-1}) of Clearwater Lake. Figures are whole-lake measurements unless otherwise noted.

Ion	1973	1974[1]	1975	Year 1976	1977	1978	1979
Ca^{2+}	6.3	5.5	5.5	6.1	5.7	5.7	6.3
Mg^{2+}	1.9	1.3	1.1	1.7	1.4	1.5	1.4
Na^{+}	1.4	1.5	1.6	1.5	1.6	1.6	1.7
K^{+}	1.3	1.0	0.86	0.72	0.72	0.66	0.70
Cl^{-}	-	1.1	1.5	1.8	2.2	3.1	3.6
$SO_4{}^{2-}$	27.8	25.6	24.9	26.0	26.4	23.9	22.0

[1] All samples from 1 m below surface.

Table 8-4. Annual average major ion content (mg L^{-1}) of Lohi Lake. Figures are whole-lake measurements unless otherwise noted.

Ion	Year						
	1973[2]	1974[1,2]	1975[2]	1976	1977	1978	1979
Ca^{2+}	6.2/9.0	7.6/8.0	6.9/8.9	8.0	7.2	6.7	6.6
Mg^{2+}	2.5/1.3	1.4/1.3	1.3/1.1	1.2	1.6	1.6	1.5
Na^{+}	1.9/1.7	1.5	1.7	1.6	1.6	1.6	1.8
K^{+}	1.3/1.1	1.0	0.85	0.75	0.76	0.70	0.75
Cl^{-}	-	1.4	2.0	2.4	3.0	4.0	4.4
SO_4^{2-}	26.7/27.3	25.9	24.0	25.0	24.8	23.7	21.4

[1] all samples from 1 m below surface.

[2] left values before neutralization, right values after neutralization.

Table 8-5. Annual average major ion content (mg L^{-1}) of Hannah Lake. Figures are whole-lake measurements unless otherwise noted.

Ion	Year 1973	1974[1]	1975[2]	1976	1977	1978	1979
Ca^{2+}	12.5	11.4	12.8/20.1	19.2	18.1	16.5	15.1
Mg^{2+}	4.3	3.6	4.3/3.8	4.1	4.8	4.5	3.9
Na^{+}	3.1	3.5	7.5/8.2	14.8	22.1	24.8	29.5
K^{+}	2.0	2.1	1.9/2.0	1.9	2.1	2.1	2.1
Cl^{-}	-	2.7	14.7/16.2	29.4	43.5	46.5	52.5
SO_4^{2-}	56.8	57.6	53.0/57.7	53.6	49.8	46.7	39.8

[1] all samples from 1 m below surface.

[2] left values before neutralization, right values after neutralization.

Table 8-6. Annual average major ion content (mg L^{-1}) of Middle Lake. Figures are whole-lake measurements unless otherwise noted.

Ion	Year						
	1973[2]	1974[1]	1975	1976	1977	1978	1979
Ca^{2+}	9.8/14.0	14.2	12.5	12.6	12.0	11.5	10.9
Mg^{2+}	5.0/3.0	2.6	3.0	3.2	3.6	3.5	3.0
Na^{+}	2.4/2.3	2.4	4.7	8.5	12.1	14.4	18.4
K^{+}	1.9/1.8	1.7	1.6	1.6	1.6	1.6	1.6
Cl^{-}	-	1.5	7.4	14.7	22.7	26.9	32.6
SO_4^{2-}	44.5/44.6	41.8	40.8	41.2	39.7	36.8	33.8

[1] all samples from 1 m below surface.

[2] left values before neutralization, right values after neutralization.

Table 8-7. Annual average major ion content (mg L^{-1}) of Nelson Lake. Figures are whole-lake measurements unless otherwise noted.

	Year						
Ion	1973	1974[1]	1975[2]	1976	1977	1978	1979
Ca^{2+}	5.0	4.4	4.1/5.0	5.3	5.0	4.7	4.7
Mg^{2+}	1.3	1.0	<1/1.0	1.0	1.1	1.0	1.0
Na^{+}	1.3	1.2	1.0/1.4	1.0	0.9	0.9	0.8
K^{+}	1.1	0.7	0.5/0.5	0.5	0.5	0.5	0.5
Cl^{-}	1.0	0.6	0.4/0.5	0.5	0.5	0.4	0.4
SO_4^{2-}	16.4	16.1	15.8/16.7	15.1	15.3	14.9	14.4

[1] all samples from 1 m below surface.

[2] left values before neutralization, right values after neutralization.

c) the SO_4^{2-} concentration in Middle Lake remained constant between 1974 and 1977, but was somewhat higher in 1973 and lower in 1978 and 1979. The SO_4^{2-} concentration in Hannah Lake declined gradually from 1974 to 1978, then substantially in 1979,

d) the Ca^{2+} concentrations increased immediately after neutralization in each lake (Chapter 6), then gradually declined.

In Nelson Lake (Table 8-7):

a) the Mg^{2+}, Na^+, K^+, and Cl^- concentrations have remained relatively constant, although the 1973 values are slightly higher than other years,

b) the SO_4^{2-} concentration remained relatively constant but may have declined in the latest years,

c) the Ca^{2+} concentrations increased immediately after neutralization, and appeared to have declined by only a small amount in the next 4 years.

Therefore, the application of a steady-state mass balance model (equation 8-3) to the Mg^{2+}, Na^+ and K^+ budgets of Clearwater and Lohi Lakes, to the Mg^{2+} and K^+ budgets of Hannah and Middle Lakes, and the Mg^{2+}, Na^+, K^+ and Cl^- budgets of Nelson Lake provides a means of testing the proposed model. That is, it can be determined whether application of the steady state model results in accurate prediction of the lakes' steady state concentrations. If the model is validated, the measured inputs and outputs for the other parameters whose concentration in the lakes is not in steady-state can be used to calculate an expected steady-state concentration. If this predicted concentration is less than the measured concentration, but the measured concentration is increasing, then an input that is either unmeasured or underestimated is probable; if the predicted steady-state is less than a decreasing measured concentration, then it is probable that a reduction in input has occurred, but the lake has not yet reached a steady-state reflecting the current inputs.

The results in Tables 8-3 to 8-7 also indicate that any changes in the chemistry of the study lakes resulting from the change in stock height and SO_2 emission levels at Copper Cliff in 1972 were realized before the start of this study (i.e. within a 2-year period). Since the response times of the study lakes are greater than 2 years (Table 8-1), these changes at the Copper Cliff smelters could not have had major impacts on the study lakes.

E. Model Validation

The mass balances for the major ions noted above are reported for the 5 study lakes in Appendix 10. Monthly inputs from each source (deposition directly on the lake, runoff from gauged and ungauged watersheds) and outputs via outflow for the period June 1977 - December 1979 are provided. Mass balances for four 12-month periods and the total 31-month period of measurement, together with the hydraulic load are summarized in Tables 8-8 to 8-12.

Summaries of the predicted steady-state concentrations of Mg^{2+}, K^{+}, Na^{+}, Ca^{2+}, Cl^{-} and $SO_4{}^{2-}$ for the five lakes based on each of the 5 time intervals are given in Tables 8-13 to 8-17 and compared to measured concentrations in the lakes at the end of the time interval (average concentration during the final month of the period).

In Clearwater and Lohi Lakes, the Mg^{2+} and K^{+}

Table 8-8. Outflow of water (Q; in L x 10^9) and input of major ions (mg x 10^9) to Clearwater Lake for 5 different time periods.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
Q	1.75	1.51	2.32	2.11	4.39
Na^+	3.91	3.22	3.54	3.44	8.59
K^+	1.11	0.80	1.17	1.18	2.48
Ca^{2+}	9.07	7.19	9.61	10.8	23.1
Mg^{2+}	1.99	1.61	2.06	2.32	4.99
Cl^-	7.89	6.62	7.46	8.14	18.6
SO_4^{2-}	32.1	25.6	35.6	40.3	83.7

Table 8-9. Outflow of water (Q; in L x 10^9) and input of major ions (mg x 10^9) to Lohi Lake for 5 different time periods.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
Q	2.78	2.06	3.11	2.73	6.21
Na^+	4.11	3.57	4.76	4.26	9.68
K^+	1.59	1.29	1.98	1.85	3.87
Ca^{2+}	12.5	10.5	15.2	14.2	30.8
Mg^{2+}	3.06	2.55	3.46	3.21	7.24
Cl^-	5.94	5.73	8.71	8.23	16.4
$SO_4{}^{2-}$	52.2	43.8	59.9	56.1	125

Table 8-10. Outflow of water (Q; in L x 10^8) and input of major ions (mg x 10^8) to Hannah Lake for 5 different time periods.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
Q	4.20	3.71	5.96	5.03	10.5
Na^+	7.53	6.24	7.08	6.21	16.5
K^+	2.17	1.59	2.59	2.50	5.03
Ca^{2+}	16.1	12.4	18.1	20.4	42.6
Mg^{2+}	3.87	3.17	4.30	4.89	10.2
Cl^-	4.04	2.98	3.41	3.08	8.37
SO_4^{2-}	76.9	63.8	87.4	99.2	205

Table 8-11. Outflow of water (Q; in L x 10^9) and input of major ions (mg x 10^9) to Middle Lake for 5 different time periods.

	June 1977–May 1978	1978	June 1978–May 1979	1979	June 1977–Dec. 1979
Q	0.93	1.11	1.59	1.41	2.67
Na^+	10.3	9.13	14.4	12.2	26.0
K^+	1.21	0.98	1.55	1.35	2.87
Ca^{2+}	10.1	8.17	11.6	10.5	23.7
Mg^{2+}	2.62	2.20	2.98	2.65	6.10
Cl^-	17.6	15.7	24.3	20.2	43.8
SO_4^{2-}	33.6	28.1	38.8	36.7	81.1

Table 8-12. Outflow of water (Q; in L x 10^9) and input of major ions (mg x 10^9) to Nelson Lake for 5 different time periods.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
Q	6.43	5.43	7.37	7.15	16.7
Na^+	6.70	6.47	7.00	6.37	15.9
K^+	1.95	1.99	2.62	2.66	5.40
Ca^{2+}	18.4	17.8	23.6	24.5	50.6
Mg^{2+}	4.18	3.74	4.59	4.71	10.4
Cl^-	2.97	2.75	3.10	3.45	7.79
SO_4^{2-}	73.0	70.7	92.4	99.6	203

Table 8-13. Half-time for lake response to change in input ($t_{1/2}$; in years, see equation 8-4), initial and final concentrations for each time period ($[X]_i$, $[X]_f$; in mg L^{-1}), and predicted steady-state concentration ($[X]_{ss}$; in mg L^{-1}) for major ions in Clearwater Lake.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
$t_{1/2}$	2.54	2.95	1.92	2.11	2.61
$[Mg^{2+}]_i$	1.45	1.4	1.45	1.35	1.45
$[Mg^{2+}]_{ss}$	1.14	1.07	0.89	1.10	1.14
$[Mg^{2+}]_f$	1.45	1.35	1.25	1.35	1.35
$[K^+]_i$	0.70	0.70	0.68	0.77	0.70
$[K^+]_{ss}$	0.63	0.53	0.50	0.56	0.56
$[K^+]_f$	0.68	0.77	0.70	0.75	0.75
$[Na^+]_i$	1.60	1.65	1.65	1.60	1.60
$[Na^+]_{ss}$	2.23	2.13	1.53	1.63	1.96
$[Na^+]_f$	1.65	1.60	1.60	1.60	1.60
$[Ca^{2+}]_i$	5.60	6.00	5.80	5.70	5.60
$[Ca^{2+}]_{ss}$	5.18	4.76	4.14	5.12	5.26
$[Ca^{2+}]_f$	5.80	5.70	5.80	6.60	6.60
$[Cl^-]_i$	2.10	2.40	2.90	3.60	2.10
$[Cl^-]_{ss}$	4.51	4.38	3.22	3.86	4.24
$[Cl^-]_f$	2.90	3.60	3.50	3.70	3.70
$[SO_4^{2-}]_i$	27.0	26.0	23.5	24.0	27.0
$[SO_4^{2-}]_{ss}$	18.3	17.0	15.3	19.1	19.1
$[SO_4^{2-}]_f$	23.5	24.0	21.5	22.5	22.5

Table 8-14. Half-time for lake response to change in input ($t_{1/2}$; in years, see equation 8-4), initial and final concentrations for each time period ($[X]_i$, $[X]_f$; in mg L^{-1}), and predicted steady-state concentration ($[X]_{ss}$; in mg L^{-1}) for major ions in Lohi Lake.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
$t_{1/2}$	0.62	0.84	0.56	0.63	0.72
$[Mg^{2+}]$ i	1.50	1.60	1.50	1.50	1.50
$[Mg^{2+}]$ ss	1.10	1.24	1.11	1.18	1.17
$[Mg^{2+}]$ f	1.50	1.50	1.40	1.50	1.50
$[K^{+}]$ i	0.70	0.75	0.73	0.73	0.70
$[K^{+}]$ ss	0.57	0.63	0.64	0.68	0.62
$[K^{+}]$ f	0.73	0.73	0.80	0.75	0.75
$[Na^{+}]$ i	1.60	1.65	1.70	2.00	1.60
$[Na^{+}]$ ss	1.48	1.73	1.53	1.56	1.56
$[Na^{+}]$ f	1.70	2.00	1.70	1.80	1.80
$[Ca^{2+}]$ i	7.00	7.20	6.60	7.20	7.00
$[Ca^{2+}]$ ss	4.50	5.10	4.89	5.20	4.96
$[Ca^{2+}]$ f	6.60	7.20	6.40	6.40	6.40
$[Cl^{-}]$ i	2.80	3.50	3.80	4.50	2.80
$[Cl^{-}]$ ss	2.14	2.78	2.80	3.01	2.64
$[Cl^{-}]$ f	3.80	4.50	4.30	4.40	4.40
$[SO_4^{2-}]$ i	24.0	24.3	21.5	23.5	24.0
$[SO_4^{2-}]$ ss	18.8	21.3	19.3	20.6	20.1
$[SO_4^{2-}]$ f	21.5	23.5	20.5	21.5	21.5

Table 8-15. Half-time for lake response to change in input ($t_{1/2}$; in years, see equation 8-4), initial and final concentrations for each time period ($[X]_i$, $[X]_f$; in mg L^{-1}), and predicted steady-state concentration ($[X]_{ss}$; in mg L^{-1}) for major ions in Hannah Lake.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
$t_{1/2}$	1.78	2.02	1.26	1.49	1.83
$[Mg^{2+}]_i$	4.70	4.88	4.63	4.45	4.70
$[Mg^{2+}]_{ss}$	0.92	0.85	0.72	0.97	0.97
$[Mg^{2+}]_f$	4.63	4.45	4.00	4.10	4.10
$[K^+]_i$	2.00	2.10	1.90	1.88	2.00
$[K^+]_{ss}$	0.52	0.43	0.43	0.50	0.48
$[K^+]_f$	1.90	1.88	2.05	2.05	2.05
$[Na^+]_i$	22.00	22.70	24.00	25.75	22.00
$[Na^+]_{ss}$	1.79	1.68	1.19	1.23	1.57
$[Na^+]_f$	24.00	25.75	27.00	31.00	31.00
$[Ca^{2+}]_i$	18.60	17.70	16.60	16.60	18.60
$[Ca^{2+}]_{ss}$	3.83	3.34	3.04	4.06	4.06
$[Ca^{2+}]_f$	16.6	16.6	15.0	15.40	15.40
$[Cl^-]_i$	43.50	43.30	45.50	46.50	43.50
$[Cl^-]_{ss}$	0.96	0.80	0.57	0.61	0.80
$[Cl^-]_f$	45.5	46.5	53.0	51.0	51.0
$[SO_4{}^{2-}]_i$	50.0	50.8	47.8	47.3	50.0
$[SO_4{}^{2-}]_{ss}$	18.30	17.20	14.66	19.72	19.52
$[SO_4{}^{2-}]_f$	47.8	47.25	39.00	46.0	46.0

Table 8-16. Half-time for lake response to change in input ($t_{1/2}$; in years, see equation 8-4), initial and final concentrations for each time period ($[X]_i$, $[X]_f$; in mg L^{-1}), and predicted steady-state concentration ($[X]_{ss}$; in mg L^{-1}) for major ions in Middle Lake.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
$t_{1/2}$	1.31	1.09	0.76	0.86	1.16
$[Mg^{2+}]_i$	3.60	3.6	3.53	3.40	3.60
$[Mg^{2+}]_{ss}$	2.83	1.98	1.87	1.88	2.28
$[Mg^{2+}]_f$	3.53	3.40	3.10	3.05	3.05
$[K^+]_i$	1.60	1.65	1.50	1.60	1.60
$[K^+]_{ss}$	1.31	0.88	0.97	0.96	1.07
$[K^+]_f$	1.50	1.60	1.60	1.60	1.60
$[Na^+]_i$	13.00	12.30	14.00	16.00	13.00
$[Na^+]_{ss}$	11.11	8.23	9.06	8.65	9.74
$[Na^+]_f$	14.00	16.00	17.00	19.00	19.00
$[Ca^{2+}]_i$	12.5	12.0	11.50	12.00	12.50
$[Ca^{2+}]_{ss}$	10.90	7.36	7.30	7.45	8.88
$[Ca^{2+}]_f$	11.50	12.00	10.60	11.20	11.20
$[Cl^-]_i$	22.50	23.5	26.00	28.00	22.50
$[Cl^-]_{ss}$	18.99	14.14	15.28	14.33	16.40
$[Cl^-]_f$	26.00	28.00	32.00	33.00	33.00
$[SO_4{}^{2-}]_i$	43.00	39.5	37.80	38.00	43.00
$[SO_4{}^{2-}]_{ss}$	36.25	25.32	24.40	26.03	30.37
$[SO_4{}^{2-}]_f$	37.80	38.00	33.50	33.50	33.50

Table 8-17. Half-time for lake response to change in input ($t_{1/2}$; in years, see equation 8-4), initial and final concentrations for each time period ($[X]_i$, $[X]_f$; in mg L^{-1}), and predicted steady-state concentration ($[X]_{ss}$; in mg L^{-1}) for major ions in Nelson Lake.

	June 1977–May 1978	1978	June 1978–May 1979	1979	June 1977–Dec. 1979
$t_{1/2}$	3.9	4.6	3.4	3.5	3.9
$[Mg^{2+}]_i$	1.15	1.25	1.00	1.00	1.15
$[Mg^{2+}]_{ss}$	0.65	0.69	0.62	0.66	0.63
$[Mg^{2+}]_f$	1.00	1.00	0.95	1.00	1.00
$[K^+]_i$	0.50	0.45	0.45	0.50	0.50
$[K^+]_{ss}$	0.30	0.36	0.36	0.37	0.33
$[K^+]_f$	0.45	0.50	0.50	0.60	0.60
$[Na^+]_i$	0.90	0.90	0.85	1.00	0.90
$[Na^+]_{ss}$	1.00	1.20	0.95	0.89	0.97
$[Na^+]_f$	0.85	1.00	0.80	0.80	0.80
$[Ca^{2+}]_i$	5.40	5.00	4.70	4.60	5.40
$[Ca^{2+}]_{ss}$	2.86	3.28	3.20	3.43	3.07
$[Ca^{2+}]_f$	4.70	4.60	4.60	4.60	4.60
$[Cl^-]_i$	0.50	0.45	0.45	0.55	0.50
$[Cl^-]_{ss}$	0.46	0.51	0.42	0.48	0.47
$[Cl^-]_f$	0.45	0.55	0.50	0.40	0.40
$[SO_4^{2-}]_i$	16.5	16.0	14.5	15.5	16.5
$[SO_4^{2-}]_{ss}$	11.4	13.0	12.5	13.9	12.3
$[SO_4^{2-}]_f$	14.5	15.5	14.0	14.3	14.3

concentrations predicted on the basis of any of the annual loads or the 31-month load are very close to the measured values. The predicted steady-state concentrations, however, are in all cases (ie. 10 individual predictions) slightly lower than the measured values. Although the difference between predicted and measured concentrations is in most cases less than the analytical precision, the bias to low predictions indicates that the errors are not random. The measured Na^+ concentrations, on the other hand, match closely the predicted steady-state levels, indicating that we have underestimated the inputs of Mg^{2+} and K^+ to each lake or that analytical methods for Mg^{2+} and K^+ at these low levels are biased.

In Hannah Lake, the measured Mg^{2+} and K^+ concentrations, although constant over the course of the study, are 5-8 times greater than the predicted steady-state levels (Table 8-15). A possible explanation for this is that the calculated terrestrial input from the Hannah Lake watershed (all of which is ungauged) was underestimated, since it was based on exports measured for the Clearwater Inlet 1 watershed . If the actual weathering rates (and therefore cation export rates) were higher at Hannah and Middle Lakes than Clearwater Lake, the expected steady-state concentrations would be underestimated. The results for Mg^{2+} and K^+ for Middle Lake support this hypothesis; the measured levels (Table 8-16) are 1 1/2 - 2 times greater than the predicted steady-state concentrations. The differences are much less than for Hannah Lake because the major input of these ions to Middle Lake, the Hannah Lake outflow, is measured rather than estimated. These results can be used in an alternate way. Calculations of total input needed to maintain the measured steady-state levels should provide someindication of the actual export rates for the Hannah and Middle Lake watersheds.

In Nelson Lake, the predicted steady-state Mg^{2+} and K^+ concentrations are again comparable to, but always lower, than the measured levels (Table 8-17), indicating that the inputs used are underestimates, that there is an analytical bias or that the model, per se, underestimates the concentrations of these parameters. The Na^+ and Cl^- steady-state predictions, on the other hand, are virtually identical to the measured concentrations. Since the mass balance model is unlikely to work for one conservative substance but not for another, the low predictions for Mg^{2+} and K^+ are probably not a result of a failure of the model, but occur either because the inputs are underestimated or the analytical procedures used are biased for particular sample types, eg. give higher results for lakewater than for precipitation samples. However, since the actual concentrations are low, the absolute differences between predicted and measured concentrations are not significant.

In summary, the measured mass balances and the steady-state version of the mass balance model (equation 8-3) provide good predictions of the concentrations in the study lakes of those elements that appear to be in steady-state. In the case of Hannah and Middle Lakes, where predicted concentrations do not agree with measured values, the input rates of Mg^{2+} and K^+ to the lakes are suspect. The model can, therefore, be used to make predictions of expected levels of other conservative substances in the same study lakes.

F. The Impact of Road Treatments on the Na^+, Cl^- and Ca^{2+} Budgets of the Study Lakes

i. Clearwater and Lohi Lakes

The Cl^- concentrations have increased continuously since 1974 in Clearwater, Lohi, Hannah and Middle Lakes (Tables 8-3 to 8-6), with increases in the latter 2 lakes being much greater than those in the former. This is undoubtedly a result of application of NaCl and/or $CaCl_2$ to roads in the watersheds for ice and dust control (see Chapter 5). The measured concentrations of Cl^- in Clearwater Lake by 1979 were comparable to the predicted steady-state values (3.7 vs. 3.9 mg l^{-1}; Table 8-13), indicating that, although the Cl^- concentration in the lake has been increasing, the increases reflect our measured input. The Cl^- export from subwatershed 2 (see Chapter 5) is exceptionally high and can, alone, account for the increases in lake concentration. In Lohi Lake, (Table 8-14) the measured Cl^- concentrations were ~50% greater than the predicted steady-state levels, indicating that excess Cl^- was being supplied directly from the Lohi Lake watershed in addition to the excess contributed via the Clearwater Lake outflow.

Although mass balance data are not available for the period June 1973 - May 1977, the input of Cl^- required to raise the lake concentrations can be roughly estimated from the non-steady state model (equation 8-2) using long-term hydrologic data (Table A3-3 Appendix 3). The average Cl^- concentration measured each year, in turn, is treated as the initial value and the input required to raise the lake concentration to that of the subsequent year in one year is calculated. Predicted total annual inputs of Cl^- are shown in Table 8-18. In Clearwater Lake, the extra Cl^- input has

Table 8-18. Input of Cl^- required to raise lake concentrations from initial ($[Cl]_i$) to final ($[Cl]_f$) levels in one year (predicted J_{Cl}), and difference between this calculated input and input required to maintain background (i.e. 1974) levels.

	$[Cl]_i$	$[Cl]_f$	predicted J_{Cl}	ΔJ[1]$_{Cl}$
	mg L^{-1}		10^9 mg yr^{-1}	
Lohi Lake[3]				
1974-75	1.4	2.0	4.89	2.16
1975-76	2.0	2.4	5.34	2.61
1976-77	2.4	3.0	6.84	4.11
1977-78	3.0	4.0	9.45 (12.5)[2]	6.72 (9.77)[2]
1978-79	4.0	4.4	9.24 (14.2)[2]	6.51 (11.5)[2]
		mean	7.15	4.42
Clearwater Lake[3]				
1974-75	1.1	1.5	4.49	2.87
1975-76	1.5	1.8	4.36	2.74
1976-77	1.8	2.2	5.52	3.90
1977-78	2.2	3.1	9.70 (10.5)[2]	8.08 (8.9)[2]
1978-79	3.1	3.6	8.15 (11.0)[2]	6.53 (9.4)[2]
		mean	6.44	4.82

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[1] input required to maintain 1.1 mg L^{-1} in Clearwater Lake is 1.62 x 10^9 mg yr^{-1}; for 1.4 mg L^{-1} in Lohi Lake it is 2.73 x 10^9 mg yr^{-1}.

[2] figures in brackets based on measured Q rather than long-term average.

[3] calculations based on mean annual Cl^- concentrations.

Table 8-19. Annual average (whole-lake) Na^+ and Cl^- concentrations in Clearwater and Lohi Lakes, increases in Cl^- (ΔCl^-) between each year, and the corresponding increase expected in Ca^{2+} concentration.

	Clearwater				Lohi			
	Na^+	Cl^-	ΔCl^-	ΔCa^{2+}	Na^+	Cl^-	ΔCl^-	ΔCa^{2+}
	($\mu eq\ L^{-1}$)			($mg\ L^{-1}$)	($\mu eq\ L^{-1}$)			$mg\ L^{-1}$
1973	61	–[2]			78	–[2]		
1974[1]	65	31			65	39		
			11	0.22			17	0.34
1975	69	42			74	56		
			9	0.18			12	0.24
1976	65	51			69	68		
			11	0.22			17	0.34
1977	69	62			69	85		
			25	0.50			28	0.56
1978	69	87			69	113		
			12	0.24			8	0.16
1979	69	99			72	121		
			$\Sigma = 68$	1.36			$\Sigma = 82$	1.64

[1] all samples from 1 m below surface.

[2] no data.

ranged from 2.7 - 8.1 x 10^9 mg yr^{-1}, averaging ~75% of the predicted total input. In Lohi Lake, the excess has been 2.2 - 6.7 x 10^9 mg yr^{-1} (average of ~60% of the predicted total input), and this has been rising as the cumulative effects of the inputs to Clearwater Lake are felt in Lohi Lake.

In both Clearwater and Lohi Lakes, the increase in Cl^- has not been accompanied by an increase in Na^+ (Tables 8-3, 8-4). The Cl^- can, therefore, be entirely attributed to $CaCl_2$ applications and the expected change in Ca^{2+} concentration can be calculated (Table 8-19). However, this is complicated by the fact that neutralization treatments used Ca compounds ($CaCO_3$, $Ca(OH)_2$), making comparison of expected change in Ca^{2+} concentration, based on postulated $CaCl_2$ inputs, with measured change impossible for Lohi Lake. For Lohi Lake, the model can be used instead to correct the neutralization treatment additions of Ca^{2+} for the extra $CaCl_2^-$-derived input. Although the expected changes in Ca^{2+} concentration are small (0.16 - 0.56 mg L^{-1} yr^{-1}), the total change (1.6 mg L^{-1} from 1974 to 1979) is significant compared to the amount added by neutralization and to the subsequent washout of Ca^{2+} each year via the outflow. The expected change in Ca^{2+} concentration in Clearwater Lake is even less (0.18 - 0.50 mg L^{-1} yr^{-1}; total of 1.4 mg L^{-1} over the period 1974 to 1979), so it is not surprising that these differences may not be distinguishable from the year-to-year variation. Nevertheless, the extra input of Ca^{2+} should be considered in the Ca^{2+} balances of the study lakes.

It is possible, using the non-steady-state version of the mass balance model (equation 8-2), to determine if the extra load of Cl^- required to raise the lakes' concentrations from the observed initial to final values for each time period (ie. over 12 or 31 months) is balanced by the extra Ca^{2+}, above the measured input, that is needed to raise the lake Ca^{2+} concentrations over the same time period. Calculations were carried out only for the periods with measured mass balance data. In Table 8-20, the extra Cl^- input (ΔJ_{Cl}) needed to attain the measured Cl^- concentrations in each lake over each time period is converted to an equivalent amount of Ca^{2+} (ΔJ_{Ca}), which is added to the measured Ca^{2+} input. This total Ca^{2+} input (ΔJ_{Ca} + measured J_{Ca}) is then compared to that needed to attain the measured concentrations (predicted J_{Ca}) as calculated by equation 8-2. In Clearwater Lake in the period 1977-78, the additional Ca^{2+}, input based on excess Cl^- input (0.93×10^9 mg), gave a total Ca^{2+} input of 10.0×10^9 mg, very close to the predicted input of 11.3×10^9 mg needed to explain the observed Ca^{2+} concentrations in the lake in this time period. Calculations for other 12-month time intervals and the entire 31-month period were not always in such good agreement, however. This may have occurred because the actual changes in lake concentrations over these shorter time periods on which these calculations are based were relatively small, so that sample variation may be important.

In Lohi Lake, the additional Ca^{2+} inputs, based on excess Cl^- inputs, increased the total Ca^{2+} input by ~25% (6.66×10^9 mg increase in a total of 37.5×10^9 mg over the 31-month period). The predicted Ca^{2+} inputs (that is, those required to attain the measured Ca^{2+} concentrations in Lohi Lake by the end of each time period) were in excellent agreement with those based on the excess Cl^- inputs, not only on the basis of a 31-month time interval, but also on the basis of the individual 12-month intervals.

Table 8-20. Comparison of the input of Ca^{2+} predicted from lake concentration with that predicted on the basis of the lakes' excess Cl input. The Cl^- input required to attain measured lake concentrations (predicted J_{Cl}) less the measured Cl^- input (measured J_{Cl}) is calculated (ΔJ_{Cl}), converted to an equivalent amount of Ca^{2+} (ΔJ_{Ca}) which is added to the measured Ca^{2+} input to give the total Ca^{2+} input (J_{Ca}). The predicted J_{Ca} is calculated as the input required to maintain measured lake concentrations. All results in 10^9 mg per time period.

	June 1977-May 1978	1978	June 1978-May 1979	1979	June 1977-Dec. 1979
Clearwater Lake					
measured J_{Cl}	7.89	6.62	7.46	8.14	18.6
predicted J_{Cl}[1]	9.54	12.3	11.4	8.35	23.4
ΔJ_{Cl}	1.65	5.68	3.94	0.21	4.8
ΔJ_{Ca}	0.93	3.21	2.23	0.12	2.71
measured J_{Ca}[1]	9.07	7.19	9.61	10.8	23.1
total J_{Ca}	10.0	10.4	11.9	10.9	25.8
predicted J_{Ca}	11.3	6.90	13.5	18.8	33.4
Lohi Lake					
measured J_{Cl}	5.94	5.73	8.71	8.23	16.4
predicted J_{Cl}[1]	11.9	10.9	14.0	11.9	28.2
ΔJ_{Cl}	5.96	5.17	5.29	3.67	11.8
ΔJ_{Ca}	3.37	2.92	2.99	2.07	6.66
measured J_{Ca}	12.5	10.5	15.2	14.2	30.8
total J_{Ca}	15.9	13.4	18.2	16.3	37.5
predicted J_{Ca}[1]	17.8	14.8	19.7	16.4	39.4

[1] initial and final concentrations used to calculate predicted input were based on mean concentrations in first and last month of each time period.

Thus, it can be concluded that the excess Cl^- input resulting from road treatments in the Lohi and Clearwater Lake watersheds is associated with Ca^{2+}, and that the measured inputs of Ca^{2+} can be corrected based on the non-steady state model.

ii. Hannah and Middle Lakes

In Hannah and Middle Lakes, the measured concentrations of Cl^- greatly exceeded the steady-state levels predicted on the basis of the measured inputs (Tables 8-15, 8-16). In Hannah Lake, measured levels were ~50-fold greater than predicted concentrations, while in Middle Lake they were ~2-fold greater. The latter figure would be much higher except for the fact that much of the excess Cl^- in Hannah Lake reaches Middle Lake via the Hannah Lake outflow (which is gauged and therefore included in the Middle Lake mass balances).

Although mass balance data are not available prior to June, 1977, the annual input of Cl^- required to raise the lakes' concentrations can be estimated from the non-steady-state model (equation 8-2) using long-term average hydrologic data (Table A3-3 Appendix 3). The Cl^- concentration measured in each year, in turn, is treated as the initial value, and the input required to raise the concentration to that of the subsequent year, in one year, is calculated (equation 8-2). Using this technique, (Table 8-21), estimates of an annual input of Cl^- to Hannah Lake range from 17.1 to 28.6×10^9 mg, with an average of 22.6×10^9 mg. This is ~60 times greater than the "measured" annual inputs of 1977-1979, which were based solely on extrapolation of measurements of unaffected areas of the Clearwater Lake watershed (see Appendix 9) and measured bulk deposition. This average is also ~25 times greater than the calculated input needed to maintain a lake concentration of 2.7 mg

Table 8-21. Input of Cl^- required to raise lake concentrations from initial ($[Cl]_i$) to final ($[Cl]_f$) levels in one year (predicted J_{Cl}), and difference between this calculated input and input required to maintain background (ie. 1974) levels (ΔJ_{Cl}).

	$[Cl]_i$	$[Cl]_f$	Predicted J	ΔJ_{Cl}[1]
	mg L^{-1}		10^9 mg yr^{-1}	
Hannah Lake[4]				
1974–75	2.7	15.4	17.1	16.1
1975–76	15.4	29.4	23.4	22.4
1976–77	29.4	43.5	28.6	27.6
1977–78	43.5	46.5	19.6	18.6[2]
1978–79	46.5	52.5	24.5	23.5[2]
		mean	22.6	21.6
Middle Lake[4]				
1974–75	1.5	7.4	14.9	13.5
1975–76	7.4	14.7	23.7	22.3
1976–77	14.7	22.7	32.3	30.9
1977–78	22.7	26.9	31.4	30.0[3]
1978–79	26.9	32.6	38.8	37.4[3]
		mean	28.2	26.8

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[1] input required to maintain 2.7 mg L^{-1} in Hannah Lake is 0.98×10^9 mg yr^{-1}; in Middle Lake for 1.5 mg L^{-1} is 1.44×10^9 mg yr^{-1}.

[2] measured input in these years ($0.34 - 0.40 \times 10^9$ mg yr^{-1}) was lower than approximated background. Thus ΔJ_{Cl}'s may be underestimates by up to 0.6×10^9 mg yr^{-1}.

[3] measured inputs cannot be used to do the above calculation because of effect of Hannah Lake.

[4] calculations based on mean annual Cl^- concentrations.

L^{-1}, the level measured in the lake in 1974 prior to known use of Cl^- on roads in the watershed. Similarly, in Middle Lake, the calculated Cl^- inputs range from 14.9 to 38.8 x 10^9 mg yr^{-1} (average 28.2 x 10^9 mg yr^{-1}), about 20-fold greater than the input required to maintain the 1974 lake concentration (1.5 mg L^{-1}). The predicted load (unlike that for Hannah Lake), actually increased steadily over the years 1974-1979. This is expected because a major source, the Hannah Lake outflow, must take several years to respond to the increased inputs to Hannah Lake itself, because of the response time of Hannah Lake. In other words, any lake upstream of Middle Lake, that also receives increased inputs, will have more effect on the downstream lake each year, until a steady-state is achieved upstream. The measured 1977-1979 inputs cannot, of course, be used for comparison with these predicted inputs, since output from Hannah Lake (and therefore some of the excess input) is included in the measurements. These results, therefore, indicate that in Hannah Lake, and probably in Middle Lake, between 95 and 98% of the total annual input of Cl^- is a result of road treatments.

In Hannah and Middle Lakes, these substantial increases in Cl^- concentration have coincided with major increases in Na^+ concentration (Tables 8-5, 8-6). However, a balance (Table 8-22) indicates that all of the Cl^- cannot be accounted for by Na^+ between 1974 and 1977. In 1977-1979 and 1978-1979, however, the Na^+ increase does account for the Cl^- in total in 3 of 4 cases (actually a slight excess of Na^+ in Hannah Lake in both years and in Middle Lake in one of the years). Since the slight excess of Cl^- (relative to Na^+) in Middle Lake from 1977 to 1978 is negligible, it is likely that in 1978 and 1979 all Cl^- increases in

Table 8-22. Annual average (whole-lake) Na^+ and Cl^- concentrations in Hannah and Middle Lakes, increases in each (ΔNa^+, ΔCl^-) from year-to-year, the differences in the increases ($\Delta Cl^- - \Delta Na^+$), and the corresponding increase expected in Ca^{2+} concentration.

	Hannah						Middle					
	Na^+	Cl^-	ΔNa^+	ΔCl^-	$\Delta Cl^- - \Delta Na^+$	ΔCa^{2+}	Na^+	Cl^-	ΔNa^+	ΔCl^-	$\Delta Cl^- - \Delta Na^+$	ΔCa^{2+}
	(μeq L^{-1})					(mg L^{-1})	(μeq L^{-1})					(mg L^{-1})
1973	134	-					104	-				
			18	-	-				0	-		
1974[1]	152	76					104	42				
			199	369	170	3.41			99	166	67	1.34
1975	351	445					203	208				
			290	383	93	1.86			165	206	41	0.82
1976	641	828					368	414				
			316	397	81	1.62			156	225	69	1.38
1977	957	1225					524	639				
			117	85	-32	-0.64			99	119	20	0.40
1978	1074	1310					623	758				
			203	169	-34	-0.68			174	160	-14	-0.28
1979	1277	1479					797	918				
	Total		1140	1400	278	5.6			693	876	183	3.7

[1] all samples from 1 m below surface.

both lakes resulted from only NaCl, while in prior years, both NaCl and $CaCl_2$ contributed. The use of both compounds for road maintenance in the watersheds is documented (S. Wilson, Ministry of Transportation and Communications, pers. comm.). Of a total increase in Cl^- concentration of 1400 μeq L^{-1} in Hannah Lake, 1120 μeq L^{-1} was associated with Na^+, leaving 280 μeq L^{-1} (20%) associated with Ca^{2+}. The expected increase in Ca^{2+} concentration over the course of the study would, therefore, be 5.6 mg L^{-1}, a substantial increase compared to the lake concentrations. This increase, however, cannot be distinguished from the additions of Ca^{2+} resulting from the neutralization treatments, but must be taken into account when the depletion rate of the added neutralizing chemicals are considered (see subsequent sections). In Middle Lake, 690 of 880 μeq L^{-1} of the increase in Cl^- concentration can be accounted for by the increasing Na^+ concentration (1974-1979), with the additional 180 μeq L^{-1}, therefore, attributable to Ca^{2+}. The expected increase, 3.7 mg Ca^{2+} L^{-1}, is again significant and must be considered when assessing the results of the neutralization experiments in Middle Lake.

Unlike the case of Clearwater and Lohi Lakes, these results cannot be verified by calculating theoretical input rates of each of Cl^-, Na^+ and Ca^{2+} to see if they balance, because mass balance measurements were not carried out while $CaCl_2$ was apparently used.

Since both Middle and Hannah Lakes were also treated with neutralizing agents containing Ca^{2+} ($CaCO_3$, $Ca(OH)_2$) prior to the mass balance measurements, the lakes' Ca^{2+} concentrations would, in the absence of other effects, decline until the original (ie. pre-neutralization treatment) concentration is attained.

Additions of Ca^{2+} resulting from $CaCl_2$ applications to the roads in the watersheds should decrease, or could even reverse this rate of decline, so must be included in the Ca balances.

G. The Ca^{2+} Budgets of the Study Lakes

i. Introduction

Modelling of the Ca^{2+} concentration of the study lakes is important for several reasons. Firstly, Ca^{2+} was a component of the neutralizing agents used in all experiments (either $CaCO_3$ or $Ca(OH)_2$). It can, therefore, be used as a conservative tracer to verify that the added quantities were distributed into the water column (see Chapter 6). Secondly, because the Ca^{2+} concentrations were in steady-state prior to neutralization (as indicated by the Hannah Lake data collected prior to neutralization in 1975), the subsequent decline in Ca^{2+} concentration in the lakes, following neutralization, is a measure of the washout rate of substances from the lake. Comparison with rates of loss of alkalinity will, therefore, indicate whether washout of the supplied acid neutralizing capacity (ANC) alone can explain the lakes' re-acidification rates. In these calculations, additional Ca^{2+} supplied via $CaCl_2$ applications to roads in the lakes' watersheds must also be considered. Finally, the Ca^{2+} content of the study lakes is largely a result of watershed weathering (ie. an acid-base reaction) (Chapter 5). The measured concentration of Ca^{2+} in the study lakes prior to any manipulation or addition (ie. at steady-state) can be used to predict the steady-state input rate. Comparison of this predicted input rate for those lakes where the mass balances are estimated rather than measured (Middle and Hannah

Lakes) will indicate whether or not these extrapolations are reasonable. A predicted input greater than the estimated input would support the hypothesis that the input of strong acid to some of the watersheds is greater than measured (Chapters 2 and 5).

ii. Clearwater Lake

In Clearwater Lake, the steady-state concentrations of Ca^{2+} predicted on the basis of the stream and bulk deposition inputs for each of the 5 time periods are slightly lower than the measured concentrations (Table 8-13). This finding supports the idea that an additional source of Ca^{2+} is contributing to the lake concentrations, as postulated in section F.

If it is assumed that the Ca^{2+} concentration of Clearwater Lake was in steady-state prior to the first measured increase in Cl^- concentration (ie. prior to 1975; Table 8-19), then a steady-state input (inflows plus bulk deposition) can be calculated using the long-term average water budget. Furthermore, if it is also assumed that:

a) the increases in Cl^- concentration were a result of $CaCl_2$ applications in the watershed,

b) the Ca^{2+} reached the lake in the same proportions as the Cl^-,

c) the increases in Ca^{2+} concentration occurred during spring runoff, when the discharge into the lake was at a maximum, and

d) these increases added to the constant steady-state input,

then, a Ca^{2+} budget can be constructed from the beginning of the study to the initiation of the measurements of the mass balances (June 1977). Using these data and the measured mass balances, predictions of the changes in Ca^{2+} concentration can be derived from the mass balance model (equation 8-2) for the period June 1973 to December 1979.

Predicted and measured concentrations are shown in Fig. 8-1. Two model results are shown for the period June 1977 - December 1979; one is based on annual calculations and one on monthly calculations. It is apparent that:

a) the measured Ca^{2+} concentration is close to, but usually slightly less than, the predicted Ca^{2+} concentration,

b) the effects of $CaCl_2$ additions are predicted to be small, and may, in fact, be analytically unmeasurable, and

c) the model used on a monthly basis results in predictions that are not significantly different from those resulting from application of the model on an annual basis.

A slight change in the assumed steady-state concentration of 1973 of from 6.0 mg L^{-1} to 5.5 mg L^{-1} with a corresponding reduction in the steady-state input provides predictions that are even closer to the measured concentrations (Fig. 8-2); therefore, predicted concentrations are sensitive to the initial concentration and estimated input rates used in the model. In any case, all of thedata sets used with the steady-state model provide predictions of the Ca^{2+} concentration in Clearwater Lake that are within the limits established by the analytical precision of the measurements made.

iii. Lohi Lake

In Lohi Lake, the steady-state concentration of Ca^{2+} predicted on the basis of the measured budgets (Table 8-14) was, as for Clearwater Lake, slightly lower than the measured concentrations. It may be argued that the higher measured levels may be the residual effects of the earlier neutralization treatments with the Ca^{2+} concentration still declining by washout, rather than the result of additional unmeasured inputs of Ca^{2+}. However, it was shown (section F) that the Cl^- concentration of Lohi Lake was increasing, while the Na^+ concentration was not (Table 8-19), indicating that there was probably an additional input of Ca^{2+} from $CaCl_2$ applications in the watershed.

The steady-state input to Lohi Lake can be calculated from the lake concentrations measured prior to the first neutralization treatment in the fall of 1973 and the long-term average water budget. If the same assumptions are made concerning $CaCl_2$ additions (Table 8-19) as were made for Clearwater Lake, and in addition, the neutralization treatments are considered to result in an instantaneous increase in Ca^{2+} concentration (Table 6-2 Chapter 6), then the mass balances approximated for the period prior to June 1977 can be combined with those measured subsequently to provide the information necessary to make predictions of the long-term trends in Ca^{2+} concentration in the lake.

The predicted and measured concentrations are shown in Fig. 8-3. Four separate predictions for the period of June 1975 to December 1979 are shown. The upper pair of lines result if it is assumed that the change in Ca^{2+} concentration attributable to the third addition of neutralizing agents was based on the theoretical dosage (3.25 mg Ca^{2+} L^{-1}), while the lower pair are based on the measured increase (2.2 mg Ca^{2+} L^{-1}) in the lakewater. The theoretical and measured increases following the 2 earlier treatments were identical (see Chapter 6). In each pair of lines, the upper line includes an increase in each spring from 1975 to 1979 attributable to $CaCl_2$, while the lower line represents the case where the only Ca^{2+} additions considered were a result of neutralization. Although the evidence indicates that additions of both $CaCl_2$ and neutralizing agents raised the Ca^{2+} concentration of Lohi Lake, it is important to model the case where only neutralizing agents are considered. $CaCl_2$ is a neutral salt and does not contribute to the lake's ANC; therefore, the lake's re-acidification rate must be independent of its addition and subsequent washout.

From Fig. 8-3, it can be seen that:

a) the predictions based on third treatments of either 3.25 or 2.2 mg Ca^{2+} L^{-1} converge within ~2 years,

b) the contributions of Ca^{2+} from $CaCl_2$ additions do not alter the predicted concentrations very substantially, and

c) the predicted and measured Ca^{2+} concentrations are quite close, although the model underestimates levels for 1978-1979 by about 1 mg L^{-1}.

The mass balance model was also used on a monthly basis for the period June 1977 - December 1979. The results, shown in Fig. 8-4, are very similar to those predicted using the annual mass balances, indicating that short-term (ie. monthly) variability cannot be very important.

The results of the mass balance modelling indicate that washout of Ca^{2+} would result in the lake's Ca^{2+} concentration approaching the steady-state level observed prior to neutralization treatments in the winter of 1977-1978. If loss of ANC was a result of only washout, then the ANC of Lohi Lake would be expected to decline to pre-neutralization levels at the same time. This is discussed more fully in subsequent sections.

iv. Hannah Lake

In Hannah Lake, the predicted steady-state concentrations of Ca^{2+} range from 3.0 to 4.1 mg L^{-1} (Table 8-15). These values were predicted from budgets (Table 8-10) that were based on measured bulk deposition and extrapolated (from Clearwater Lake) input from the terrestrial watershed for the periods between June 1977 and December 1979. They are much lower than the concentrations measured either during the same time period or prior to the neutralization treatment. The concentrations measured in the later period may reflect residual effects of the neutralization treatment; however, the concentrations measured (~12 mg Ca^{2+} L^{-1}) between June 1973 and May 1975 appear to represent the steady-state condition. The input required to maintain this pre-neutralization steady-state level (4.54×10^9 mg yr^{-1}) is much greater than that measured in June 1977 - December 1979 ($1.2 - 2.0 \times 10^9$ mg yr^{-1}). Therefore, in addition to the extra Ca^{2+} supplied by neutralization treatments and by $CaCl_2$ (see section F), there is an additional unmeasured major input of Ca^{2+}.

The same is true for Mg^{2+} and K^+ (section E), and, as can be seen from Tables 8-5 and 8-15, for Na^+. That is, the current input of Na^+, based partially on extrapolation of the Clearwater Lake budget, cannot support the Na^+ concentrations measured in Hannah Lake in 1973 and 1974, prior to the first additions of NaCl in the watershed.

Therefore, the total inputs of the major cations (Ca, Mg, Na, K) to Hannah Lake are underestimated when derived by extrapolation of the Clearwater Lake budget. This supports the contention that the input of strong acid (particularly sulphuric acid) to the Hannah Lake watershed is underestimated (discussed in subsequent sections).

The Ca^{2+} concentration of Hannah Lake can be predicted using the mass balance model, if the same assumptions concerning the use of long-term average water budgets and the addition of neutralizing agents (Table 3-1) and $CaCl_2$ (Table 8-22) are made as was the case for Clearwater and Lohi Lakes. In addition, the steady-state input calculated from the 1973-1975 lake concentrations must be used for the entire study period (up to December 1979), since the "measured" budgets of June 1977-December 1979 are underestimates.

Predicted and measured Ca^{2+} concentrations are shown in Fig. 8-5. Also shown are the predictions based on the "measured" budget for the latter part of the study, which again clearly indicate that this budget is underestimated, since the concentration is predicted to drop far below the measured levels. The use of the steady-state input, on the other hand, results in predicted concentrations that are very close to those measured. This indicates that Ca^{2+} is behaving as a conservative substance, with its loss from the lake governed by washout.

Predictions including a $CaCl_2$ component differ from those based on only $CaCO_3$ and $Ca(OH)_2$ by ~2 mg Ca^{2+} L^{-1}. The measured concentrations fall between the 2 predictions, making it impossible to determine if one approach is better than the other.

The model predictions that exclude $CaCl_2$ indicate that the Ca^{2+} concentration of Hannah Lake should not have returned to the pre-neutralization steady-state by the end of the study. Extrapolation of the results indicates that the Ca^{2+} concentration will return to within 5% of the steady-state level by the summer or fall of 1982. Therefore, washout of residual ANC alone should not result in the re-acidification of Hannah Lake until this time.

v. Middle Lake

In Middle Lake, the situation is similar to that in Hannah Lake. The steady-state concentrations of Ca^{2+} prediction on the basis of the measured budgets (June 1977-December 1979) are less than those measured during this period (Table 8-16), but this again may result from residual effects of the neutralization treatment. The predictions are also, in 4 out of 5 cases, less than the steady-state concentration (9.8 mg Ca^{2+} L^{-1}) measured prior to the neutralization treatment in 1973, but the differences are much smaller than in the case of Hannah Lake, because the Hannah Lake outflow (measured) is a major input to Middle Lake.

These results indicate that, in addition to the extra Ca^{2+} supplied in the neutralization treatment (Table 3-1) and as $CaCl_2$ (section F, Table 8-22), Ca^{2+} is supplied to Middle Lake at levels above that indicated in the mass balances of 1977-1979. This also appears to be true for Mg^{2+} and K^+ (Tables 8-6, 8-16), but cannot be verified for Na^+ because of the elevation of Na^+ concentration in Hannah Lake resulting from road salt (NaCl) applications, and the subsequent elevation of input of Na^+ to Middle Lake via the Hannah Lake outflow. Nevertheless, these results again support the contention that the input of strong acid to the Middle Lake watershed is underestimated.

If the same assumptions are used as those made for the other lakes (including the use of the predicted steady-state input calculated from the pre-neutralization data for the entire study period), Ca^{2+} concentration in Middle Lake over the whole study period can be predicted. Predicted and measured concentrations are shown in Fig. 8-6, with those based on inclusion of the $CaCl_2$

additions, being 1-2 mg L^{-1} greater than those based on only neutralization additions. Again, the predicted and measured concentrations are very similar, indicating that loss of Ca^{2+} is governed by washout only.

Predicted concentrations, based on the measured inputs for the period June 1977-December 1979, are also shown in Fig. 8-6. These predictions suggest that the concentrations should decline to levels substantially below those either measured or predicted on the basis of the steady-state input.

These results (excluding the $CaCl_2$ effects) indicate that the Ca^{2+} concentration of Middle Lake should have returned to within 5 of the original steady-state by approximately the winter of 1978-1979. A comparison of this finding with the loss rate of ANC is included in subsequent sections.

vi. Nelson Lake

In Nelson Lake, the predicted steady-state Ca^{2+} concentrations were lower than the measured concentrations (Table 8-17), probably because of the effect of the neutralization treatments in 1975 and 1976. These predicted steady-state levels were comparable to the measured concentrations prior to the first treatment.

Predictions based on the mass balance model are compared to measured concentrations in Fig. 8-7. Since there was no evidence of $CaCl_2$ utilization in the lake's watershed, only the 2 neutralization treatments resulted in incremental additions of Ca^{2+}. It is evident from Fig. 8-7 that the measured annual and monthly inputs result in virtually identical predictions of Ca^{2+} concentration, and that both of these predictions match the measured concentrations very closely. The concentration declined gradually after the neutralization treatments, but because of the long response time of Nelson Lake (Table 8-1), the pre-treatment concentrations were not reached by the end of 1979. Washout of residual ANC supplied by the treatments is therefore not expected to be complete.

H. Alkalinity and the Rates of Acidification of the Study Lakes

i. Alkalinity, Acidity and pH

A detailed discussion of the theory of pH, alkalinity and acidity, and their measurement in natural waters is given in Garrels and Christ (1965), and Stumm and Morgan (1970) and will not be repeated here. Alkalinity and acidity are defined rigorously by the relationships shown in Fig. 8-8 and 8-9. The importance of pH is a result of the fact that most reactions in aquatic systems (both inorganic and biochemical) are sensitive to changes in hydrogen ion concentration; hence, pH is considered to be a controlling or "master" variable in natural waters.

a. Alkalinity

The acid neutralizing capacity (ANC) of an aqueous solution is the equivalent sum of all the bases that can be titrated with a strong acid to a pre-defined equivalence point (Stumm and Morgan 1970). At the equivalence point (i.e. where the acid neutralizing capacity = 0), a reference level of protons is defined by the proton condition, a combination of mass balance and charge balance. The acid neutralizing capacity, in effect, is a measure of the concentration of species containing protons in deficiency of the reference level minus those containing protons in excess, i.e. it is the net deficiency of protons.

Since most natural waters are closely approximated by dilute aqueous carbonate solutions, their acid neutralizing capacity (which is called alkalinity) is measured with respect to a reference level of protons defined by a pH equal to that of a solution of H_2CO_3 (= H_2CO_3 + CO_2 (aqueous)), which has a total dissolved inorganic carbon content (C_T) equal to $[H_2CO_3\ ] + [HCO_3^-] + [CO_3^{2-}]$. Other acid-consuming substances found in natural, fresh waters (eg. NH_3, borate ($B(OH)_4^-$), organic compounds) rarely contribute significantly to alkalinity.

It is important to note that the pH of the end-point of the alkalinity titration is a function of C_T and that the value of 4.5 frequently used for this end-point in the determination of alkalinity (ie. TFA) is that of a system in equilibrium with solid calcium carbonate and atmospheric CO_2. For Precambrian waters, in particular, this assumption is not valid and alkalinities measured to this end-point will be overestimates. A simple technique for revising incorrectly measured alkalinities is outlined in Appendix 1.

b. Acidity

In the case where sample pH is less than the proton reference level (ie. the end-point pH), a negative acid neutralizing capacity is obtained, which is equivalent in magnitude to the mineral acidity.

Titration upwards to the $HCO_3^- - CO_3^{2-}$ equivalence point (pH ~8.3) is, in most natural waters, a measure of the "CO_2-Acidity"; however, the chemical composition of the Sudbury study lakes is atypical (see Chapter 2). Acids other than H_2CO_3 and H^+ contribute to the acidity, and therefore, to the water's base neutralizing capacity (BNC; see Chapter 6). At the low pH of Clearwater Lake, or Hannah, Middle and Lohi Lakes prior to their neutralization, Al^{3+} contributes substantially to the measured

"CO_2- Acidity" by reacting with added OH^- in the titration. Other metals existing in the ionic form at the low pH's (Cu^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}) may also contribute base neutralizing capacity. Following lake neutralization, the metals contribute little or nothing to the measured acidities because their speciation is altered (Chapter 6). Interpretation of acidity data for the neutralized lakes is thus more straightforward than that for the acidic lakes.

c. Model Expectations

In this section, the emphasis is placed on modelling alkalinity or ANC rather than acidity or pH. Unlike pH, alkalinity is pressure and temperature independent (Stumm and Morgan 1970). The mass balance model tested and validated with other conservative elements (Mg, K, Cl, etc.) for these study lakes is suitable for ANC. The rate of loss of acid neutralizing capacity is, in effect, the rate of acidification of the lake. Since pH is a complex, non-conservative parameter, changes in pH do not linearly reflect the rate of acidification. The prediction of either the acceptable input of strong acids that would not re-acidify the neutralized lakes, or of the re-acidification rate (ie. the effective duration of the neutralizing treatment) of the lakes at the current input rates of strong acids is the ultimate purpose of the mass balance model. These predictions can be best made on the basis of an alkalinity model that can predict the loss of all ANC in a lake.

ii. Data Sources

Because of the problems with methodologies, logistics etc., almost no alkalinity measurements were made using the accurate equivalence-point Gran titration technique. Total inflection-point alkalinity mass balances, and even the lake concentration data required for model testing, are sparse or non-existent. However, by making certain approximations and estimations using other parameters, an expanded data base has been obtained. Data from the following sources have been used in the subsequent calculations and model testing:

1. Inflection-point alkalinity (TIA) was measured on a few occasions in the study lakes in 1978 and 1979. These data are the most accurate measurements available.
2. TIA was calculated from the titrations of the study lakes done in 1973 to estimate quantities of neutralizing agents required for treatment in each lake. These few data form the basis for most of the modelling done for the lakes in the 1973-1977 period, prior to measurement of any mass balances. No TIA measurements of the inputs to the study lakes (streams, precipitation) were made.
3. Alkalinities measured to a fixed end-point (TFA) were corrected (see Appendix 1) to give estimated TIA alkalinities. These data were extensively used for both mass balance calculations and as lake concentration measurements. However, this correction technique is only valid if a non-zero TFA was actually measured; that is, in cases where the sample pH was greater than the titration-endpoint (pH 4.5). The technique is, therefore, valid for all of the neutralized lakes (as long as they did not re-acidify) and all of the streams with positive TFA values, but not for acidic (pH <4.5) lake, stream or precipitation samples.
4. At low pH (<4.5 to 5.0), TIA is negative, ie. the sample has mineral acidity. In these cases, alkalinity can be approximated as $-[H^+]$.

The definition of alkalinity is:

$$[TIA] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \qquad (8\text{-}5)$$

From consideration of the carbonic acid-bicarbonate - carbonate dissociation constants, it can be shown that at low pH (ie. high $[H^+]$), only H^+ contributes significantly to the alkalinity. The other 3 components are unimportant. Estimation of TIA by this method is particularly suited to calculation of the input via atmospheric deposition. Aluminum (and other metals) may contribute to the mineral acidity at very low pH since $Al(OH)^{2+}$ present at the titration equivalence point is converted to Al^{3+} at lower pH. However, this correction has been ignored in the following calculation because it is small.

5. TIA can be approximated when inorganic carbon and CO_2^- acidity have been measured since:

$$[CO_2\text{-Acidity}] = [H_2CO_3] - [CO_3^{2-}] + [H^+] - [OH^-] \qquad (8\text{-}6)$$

$$\text{and } C_T \text{ (or DIC)} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (8\text{-}7)$$

$$\text{then } [TIA] = C_T - [CO_2\text{-Acidity}] \qquad (8\text{-}8)$$

This relationship is valid if the CO_2-acidity measurement was not influenced by the presence of strong acids (eg. sample pH >~5). On the other hand, in the case of acidic waters (pH <~5), the measured CO_2-Acidity must be corrected to account for the presence of base neutralizing components other than H_2CO_3 or HCO_3^-.

Aluminum is one potential component. As a first approximation corrections can be made as follows:

$$[\mathrm{CO_2\text{-}Acidity}] = [\mathrm{measured\text{-}Acidity}] - 4[\mathrm{Al}^{3+}]$$

where the units are in moles L^{-1}. Each mole of Al^{3+} consumes 4 moles of base when the pH is raised from ca. 4.5 to 8.3.

For acidic waters, it is not necessary that C_T be measured, because virtually all of the C_T must be as H_2CO_3* ($=H_2CO_3 + CO_2$ (aq)), and if equilibrium with the atmosphere is assumed, this is governed by the partial pressure of atmospheric CO_2:

$$[H_2CO_3*] = pCO_2 . pK_H \tag{8-9}$$

where K_H is Henry's Law constant and $pK_H = 1.41$ at 20°C. Therefore $C_T \sim 12$ μeq L^{-1}. The amount of C_T may be reduced by primary production during the daylight hours or supersaturated during periods when respiration is high. Nevertheless, $C_T = 12$ μeq L^{-1} is a reasonable approximation, since C_T is low in any case.

iii. Clearwater Lake

Clearwater Lake, the "control" lake among the study lakes, has remained acidic over the course of the study with the annual average pH ranging between 4.10 (1977) and 4.47 (1979). The TIA fluctuated between -30 and -90 μeq L^{-1} in 1973, the only year when alkalinity titrations were performed, with the average (-50 μeq L^{-1}) corresponding to a pH of 4.30, in good agreement with the measured mean pH of 4.29.

Of the 4 tributaries draining into Clearwater Lake, 2 always had pH's below the expected equivalence point of an alkalinity titration (Chapter 5). Bulk deposition samples similarly contained mineral acidity on all occasions (Chapter 2). To demonstrate that it is incorrect to simply set alkalinity equal to zero in cases where no positive alkalinity could have existed, the alkalinity model first employed only the measured alkalinity budgets for Clearwater inflows 1 and 4 (ALK 1; Table 8-23). In this case, the model predicts (Fig. 8-10) that the alkalinity of Clearwater Lake should have gradually increased from 1973 to the present, and should be, by the end of 1979, close to 0. These predictions are not supported by the available data. The pH has not increased to near the expected titration equivalence point (~5.0), with the mineral acidity remaining 3-5 times greater than predicted by the model.

For subsequent uses of the model, the alkalinity mass balance was modified. Inputs from Clearwater inflows 2 and 3 and bulk deposition were estimated from pH measurements. Inputs from inflows 1 and 4 were measured or, if <0, estimated from pH measurements. The TIA input to Clearwater Lake calculated in this way was negative rather than positive, as was the case for ALK 1.

The input required to maintain a steady-state alkalinity of $-50\ \mu\text{eq}\ L^{-1}$ is -3.67×10^9 mg yr^{-1} (calculated from equation 8-3 and assuming Q is the long-term average), a number that is close to the measured input in the period June 1977 - May 1978 (-4.28×10^9 mg), suggesting that the lake's alkalinity has not changed substantially over the course of the study.

Three variations of the inputs to the mass balance model were used (details in Table 8-23). The first (ALK 2) used inputs measured in 1977-1978 (ie. prior to shutdown) for the 1973-1977 period, the second (ALK 3) assumed that a steady-state TIA concentration existed in 1973, from which a steady-state input could be calculated and used, while the third (ALK 4) repeated ALK 3, but utilized the mass balance model on a monthly rather than annual

Table 8-23. Description of the TIA and hydrologic data used in the mass balance model for Clearwater Lake.

ALK 1: A whole-lake alkalinity mass balance was calculated using measured alkalinity budgets for Clearwater inflow 1 and inflow 4. Inputs from Clearwater inflows 2 and 3 and bulk deposition were assumed to be 0.

June 1973-May 1977 - The mass balance for June 1977-May 1978 was used for this 4-year period. The long-term Q (Appendix 3) was used. The initial alkalinity was set at -50 μeq L^{-1}. J and Q were treated as annual numbers.
June 1977-December 1979 - Measured J and Q were used. The model was run on an annual basis. The initial alkalinity was that predicted for May 1977.

ALK 2: Alkalinity for the Clearwater inflows and bulk deposition was measured or calculated as $-[H^+]$ when the measured alkalinity was $\leqslant 0$ for the period June 1977-December 1979.

June 1973-May 1977 - The alkalinity budget calculated for June 1977-May 1978 was used for this period with the long-term Q. The initial alkalinity was -50 μeq L^{-1} and the model was run on an annual basis.
June 1977-December 1979 - Measured J and Q were used with the model run on an annual basis. The initial alkalinity concentration was that predicted for May 1977.

ALK 3: The alkalinity of Clearwater Lake was assumed to be in steady-state in 1973. Using the long-term Q, the steady-state input was calculated (-3.67×10^9 mg yr^{-1}). The model was run on an annual basis.

June 1973-May 1977 - The steady-state J and the long-term Q were used with an initial alkalinity of -50 μeq L^{-1}.
June 1977-December 1979 - The measured J (as for ALK 2) and measured Q were used with the initial alkalinity at -50 μeq L^{-1} (ie. the steady-state concentration).

ALK 4: ALK 4 was identical to ALK 3 except that the model was employed on a monthly basis when measured data were available (June 1977-December 1979).

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basis for the period June 1977-December 1979.

Predictions of lake alkalinity based on the 3 modified versions of the mass balance are shown in Fig. 8-11. It is apparent that a) all 3 make very similar predictions, and that b) all predict that the calculated steady-state input and the measured input (1977-1979) should not result in any major change or shift in the lake's alkalinity. Predictions of all 3 models fall within the considerable scatter in the lake alkalinities. The variation in lake alkalinities is large, which probably reflects the fact that most values were estimated from lake pH, or acidity and aluminum concentrations. Measured TIA or TFA alkalinity values were available for 1973 only.

In summary, the measured negative input of alkalinity (or positive input of mineral acidity) is sufficient to maintain Clearwater lake at about the measured alkalinity (~-50 μeq L^{-1}), and there is no apparent reason for the pH to increase. Since the input of alkalinity from the terrestial watershed is <0 (i.e. there is a net input of mineral acidity - Appendix 10), a decrease in atmospheric deposition of strong acid cannot result in positive alkalinites in the lake unless the decrease in deposition of acid results in a generation of alkalinity >0 from the watershed. Because the response of the watershed to a change in loading of strong acid is not known, the possibility of such a change in alkalinity cannot be ascertained.

iv. Lohi Lake

Prior to the first neutralization treatment in November 1973, measurements of the TIA in Lohi Lake varied from -30 to -80 μeq L^{-1}. Conversion of lake pH measurements suggested that 40 to 50 μeq L^{-1} was a good estimate of mineral acidity. The input required to maintain -50 μeq L^{-1} as a steady-state TIA concentration is -4.88×10^9 mg yr^{-1} (calculated using equation 8-3 and long-term Q), not very different from the measured inputs in 1977-1979 (-5.08×10^9 mg from June 1977 - May 1978; -5.56×10^9 mg from June 1978 - May 1979). These measured alkalinity inputs were modified in the same way as those of Clearwater Lake to include mineral acidity in the calculation of negative alkalinity. The input of alkalinity (and therefore of mineral acidity) has apparently not varied substantially over the 7-year study period.

Model predictions based on ALK 2, ALK 3 and ALK 4 (details in Table 8-24) are shown in Fig. 8-12. ALK 1 was not used for the reasons discussed earlier. The 3 subsequent model calculations differ only in that either the measured input for the period June 1977 - May 1978 was extrapolated back to June 1973 (ALK 2), the calculated steady-state input was used from June 1973 to the time (June 1977) at which measurement of budgets began (ALK 3), or the final 31-month period was modelled on a monthly basis (ALK 4) rather than on an annual basis (ALK 3). In each case, the calculations were carried out up to the times of the addition of neutralizing chemicals (Nov. 1973, July 1974, June 1975), at which point they were re-initialized using measured lake concentrations.

The predictions based on the 3 calculations are remarkably similar, with variations between them always <10 μeq L^{-1} and usually <5 μeq L^{-1}. These differences are, of course, much smaller than the differences attributable to analytical precision. It is, therefore, effectively impossible to determine if any of the calculations make more accurate predictions than the others.

The measured or calculated alkalinities for Lohi Lake are also shown in Fig. 8-12. TIA values were calculated for 1973 from

Table 8-24. Description of the TIA and hydrologic data used in the mass balance model for Lohi Lake.

ALK 2: A whole-lake alkalinity mass balance was calculated using $-[H^+]$ for the Clearwater outflow and for bulk deposition from the atmosphere, and using ALK 2 inputs from Clearwater 1 to calculate the contribution from the ungauged area of the Lohi Lake watershed.

June 1973-November 1973 - The input calculated for June 1977-May 1978 was used for this period with the long-term Q. The initial alkalinity was set at -60 μeq L^{-1} and the model run on an annual basis.

November 1973-July 1974 - The model was re-initialized with alkalinity set at +50 μeq L^{-1} (because of the neutralization treatment), with other parameters unchanged.

July 1974-June 1975 - The model was re-initialized with alkalinity set at +20 μeq L^{-1} with other parameters unchanged because of the second neutralization treatment.

June 1975-May 1977 - The model was re-initialized with alkalinity set at +80 μeq L^{-1} and other parameters unchanged.

June 1977-December 1979 - Measured J and Q were used with the initial alkalinity that was predicted for May 1977. The model was used on an annual basis.

ALK 3: The alkalinity of Lohi Lake was assumed to be in steady-state in 1973. The steady-state input was calculated (-5.86×10^9 mg yr^{-1}) using the long-term Q. The model was used in a manner analogous to ALK 2 except that the steady-state J was used up to June 1977 instead of the measured 1977-78 J.

ALK 4: ALK 4 was identical to ALK 3 except that the model was employed on a monthly basis from June 1977-December 1979.

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the titration data used to determine treatment dosage. Results were comparable to those estimated from lake pH (ie. mineral acidity = 10^{-pH}). Most of the data in Fig. 8-12 are corrected TFA values which were measured from 1974-1979. Although these data show considerable scatter, the trend, particularly following the third neutralization treatment, is evident. Alkalinities predicted from lake pH following the re-acidification of Lohi Lake (1978, 1979) are in good agreement with the corrected TFA's. Alkalinities calculated on the basis of measured CO_2-Acidities and C_T, however, have a great deal of scatter and do not correspond closely to other alkalinity measurements in time periods where more than one method could be employed.

Lohi Lake re-acidified in the spring of 1977, following its final treatment in June 1975; that is, sometime between March and May, 1977 the alkalinity became negative. At this time, the pH dropped to ~5.0. The alkalinity has remained at ~-10 to -20 μeq L^{-1} over the following 3 years. All of the calculations using the models (Alk 2, Alk 3, Alk 4) predict that the lake should have become acidified in the late summer of 1976, and should have fluctuated around -40 μeq L^{-1} in 1978-1979; that is, it should have re-acidified 6-9 months before it did and should have 20-30 μeq L^{-1} less alkalinity than measured.

On the other hand, the calculations based on the mass balances for Ca^{2+} (Section G; Fig. 8-4) indicated that the Ca concentration would have declined to approximately the pre-neutralization steady-state level by about the early spring of 1978 (or possibly a little earlier because of the additions of $CaCl_2$). The measured Ca concentrations declined even more slowly, reaching ~6 mg L^{-1} in the spring of 1979.

The Ca results indicate that Lohi Lake re-acidified faster than would be predicted on the basis of simple washout of the residual alkalinity (equal to the washout of the conservative substance Ca). However, the rate was slower and the extent less than that predicted on the basis of calculations treating alkalinity (or, in effect, mineral acidity) as a conservative substance with sources of only the lake's watershed and precipitation falling directly on the lake. In other words, there must be an additional source of alkalinity (>0) that has slowed the re-acidification rate and resulted in a steady-state alkalinity concentation that is higher than predicted. Possible explanations for this "extra" alkalinity are discussed in subsequent sections.

v. Hannah Lake

Hannah Lake was treated with neutralizing agents in the summer of 1975. Prior to this time, the alkalinity, either measured or estimated from pH measurements, was -30 to -90 μeq L^{-1}. The input required to maintain an estimated mean steady-state alkalinity of -60 μeq L^{-1} is -1.09×10^9 mg yr^{-1} (using long term Q, calculated from equation 8-3).

Because Hannah Lake has no gauged or calibrated watersheds, its material budget must be less precise than those of the other study lakes. Alkalinity (or mineral acidity) input was estimated for the terrestrial component by extrapolation of data collected for the gauged tributary of Middle Lake (Appendix 10). Input directly to the lake surface was calculated from pH data of bulk deposition. The alkalinity input estimated in this way for the June 1977 - December 1979 period (-1.71×10^9 and -1.25×10^9 mg yr^{-1} for 1977-1978 and 1978-1979, respectively) was greater in absolute terms (ie. the mineral acidity was higher) than that based on the steady-state lake calculations. However, calculation of input on a calendar year basis (-1.10 and -1.27 x 10^9 mg yr^{-1} for 1978 and 1979, respectively) indicates that the input predicted on the basis of the steady-state assumption is not significantly different from that estimated for 1977-1979.

Model predictions based on the 3 mass balance calculations (details in Table 8-25) are shown in Fig. 8-13. As for Lohi lake, the 3 predictions are very similar with a maximum spread of only 10-15 µeq L^{-1}. All 3 calculations predict that Hannah Lake would have re-acidified in the winter of 1977-1978 or spring of 1978, a change which did not occur. Measured or calculated alkalinities are also shown in Fig. 8-13. In 1978 and 1979, alkalinity was measured by titration; these data are the most accurate available. Additional measurements (from 1975-1979) based on corrected TFA are included. These appear to be consistent with the titration alkalinities on the few occasions when there was overlap. Estimations based on CO_2-Acidity and C_T, however, again appear to be very inconsistent and are excluded from the following considerations. No calculations based on lake pH could, of course, be carried out subsequent to the neutralization, since Hannah Lake did not re-acidify in the course of the study.

The measured alkalinities clearly indicate that the alkalinity of Hannah Lake declined from the time of treatment in 1975 to the summer of 1976, but increased significantly in every year from 1976 to 1979. The first increase coincides with the addition of phosphorus to Hannah Lake. By the fall of 1978, the alkalinity was equal to that in the lake immediately following neutralization, while in 1979 it actually exceeded the value for 1975 (120 µeq L^{-1}). It can be concluded that there is a net input

Table 8-25. Description of the TIA and hydrologic data used with the mass balance model for Hannah Lake.

ALK 2: A whole-lake alkalinity mass balance was calculated using $-[H^+]$ for bulk deposition from the atmosphere. The Middle Lake inflow 1 alkalinity budget (calculated as $-[H^+]$) was used (prorated on an areal basis) to calculate the input from Hannah Lake's terrestrial watershed.

June 1973-June 1975 - The input calculated for June 1977-May 1978 was used with the long-term Q. The initial alkalinity was set at -60 μeq L^{-1} and the model run on an annual basis.

June 1975-May 1977 - The model was re-initialized with alkalinity equal to +120 μeq L^{-1} because of the neutralization treatment with other parameters unchanged.

June 1977-December 1979 - Measured J and Q were used with the initial alkalinity that was predicted for May 1977. The model was run on an annual basis.

ALK 3: The alkalinity of Hannah Lake was assumed to be in steady-state from June 1973-June 1975 when it was altered by the neutralization treatment. With the long-term Q, the steady-state input was calculated as -1.09×10^9 mg yr^{-1}. The model was used in a manner analogous to ALK 2 except that the steady-state J was used up to June 1977 instead of the measured J for June 1977-May 1978.

ALK 4: For the period June 1977-December 1979, the model was run on a monthly basis with other factors identical to ALK 3.

or production of positive alkalinity; that is, the unmeasured input or production of alkalinity is greater than the input of mineral acidity as estimated in the mass balance. The source of the extra alkalinity is discussed in a subsequent section.

The difference between predicted (from ALK 4) and measured alkalinities in the summer of 1978 reached ~110 μeq L^{-1}, while in 1979, it approached 200 μeq L^{-1}.

In summary, the Ca^{2+} mass balance and model predictions indicated that Hannah Lake's Ca^{2+} concentration would not approach the pre-treatment level until about 1982, while the alkalinity model predicts a much more rapid return to pre-treatment lake chemistry (re-acidification by the spring of 1978). The measured alkalinity, however, increased continuously following phosphorus additions.

vi. Middle Lake

Middle Lake, like Lohi Lake, was treated with neutralizing agents in the fall of 1973 (see Chapter 6), raising the alkalinity from ~-40 μeq L^{-1} to +120 μeq L^{-1}. The alkalinities measured by titration in 1973 were similar to those predicted on the basis of lake pH, although there was a 2 to 3-fold spread over the 5-month period where measurements were available (Fig. 8-14). The input required to maintain an average alkalinity of -40 μeq L^{-1} is -1.92×10^9 mg yr^{-1} (based on the long-term water renewal time for Middle Lake). This calculated input cannot be compared to the inputs measured in subsequent years (1977-1979) because the input from the Hannah Lake outflow was affected by the neutralization of Hannah Lake, the only time in this study where the chemistry of an "upstream" lake was altered.

Calculation of the alkalinity budget of Middle Lake was complicated by the treatment of Hannah Lake. Measurements made in

1977-1979 were not applicable to the pre- June 1975 period. Inputs calculated from steady-state assumptions in 1973 were not applicable after the neutralization of Hannah Lake in 1975, because the Hannah Lake outfow is a major input to Middle Lake. Therefore, the alkalinity budget for Middle Lake was calculated differently than that for the other study lakes. For the period prior to the first measured budgets, it was assumed that the alkalinity concentration of the Hannah Lake outflow was identical to that of the lake, which was predicted using the model calculations. These data were combined with the Hannah Lake outflow hydrologic data (long term Q) to provide an estimate of the input from Hannah Lake to Middle Lake. Alternatively, the measured alkalinity concentrations in Hannah Lake could have been equated to the outflow concentrations for the 1973-1977 period, but these measurements were a) too infrequent, and b) similar to the predicted concentrations in the lake.

Model predictions based on the 3 mass balance calculations (details in Table 8-26) are shown in Fig. 8-14. As in all previous cases, predictions based on all 3 calculations were very similar, with a range always <15 μeq L^{-1} and usually <10 μeq L^{-1}. These calculations indicate that the ANC of Middle Lake was expected to decline rapidly from November 1973 to June 1975, when Hannah Lake was neutralized, then decline at a much slower rate, being re-acidified between June 1976 (ALK 2) and January 1977 (ALK 3 and ALK 4). The alkalinity was predicted to fluctuate between -15 and +5 μeq L^{-1} between the summer of 1977 and December 1979. Measured lake alkalinities, based on some titrations in 1978 and 1979, and on corrected TFA in 1974-1979, are greater than the predicted values. The scatter is great in 1974 and early 1975, but alkalinity appears

Table 8-26. Description of the TIA and hydrologic data used with the mass balance model for Middle Lake.

ALK 2: An alkalinity budget was calculated for Middle Lake for June 1977-December 1979 using $-[H^+]$ (ie. pH) measurements for Middle Lake inflow 1, prorating these results on an areal basis for the remainder of the terrestrial watershed, and using $-[H^+]$ for bulk deposition directly on the lake surface. For the input from Hannah Lake outflow, measured alkalinities were used from June 1977-December 1979. Because of the neutralization treatment of Hannah Lake, these measurements cannot be utilized, at least not prior to June 1975. For the period June 1973-May 1977, monthly inputs from the Hannah Lake outflow were calculated by multiplying 1/12 of the long-term annual Q by the Hannah Lake alkalinity concentration as predicted from the model (ALK 2) for Hannah Lake. Seasonal variability in runoff was not considered.

June 1973-November 1973 - The input calculated for June 1977-May 1978 with the exception of the input from the Hannah Lake outflow (calculated as described above) was used with the long-term Q and an initial alkalinity of -40 $\mu eq\ L^{-1}$. The model was run on an annual basis.

November 1973-May 1977 - The model was run as above with initialization at +120 $\mu eq\ L^{-1}$ because of neutralization treatment.

June 1977-December 1979 - Measured J and Q were used with the initial alkalinity that was predicted for May 1977.

ALK 3: The alkalinity of Middle Lake was assumed to be in steady-state in 1973, with the calculated input being -1.92×10^9 mg yr^{-1}. The calculations were done in a manner analogous to ALK 2 except that this steady-state input was used from June 1973-June 1975. From June 1975-May 1977, calculations were similar to those of ALK 2 except that the input from the Hannah Lake outflow was calculated using Hannah Lake alkalinity concentrations predicted from ALK 3. The model was run on an annual basis.

ALK 4: ALK 4 was identical to ALK 3 except that for the period June 1975-May 1977, the input of alkalinity from the Hannah Lake outflow was calculated from Hannah Lake concentrations predicted by ALK 4 and that for the period June 1977-December 1979, the model was run on a monthly basis.

to be at a maximum at this time. The lower values recorded in 1975 remained approximately constant at ~+40 μeq L^{-1} through the end of 1977, then rose in the final 2 years to the range of +50 to +90 μeq L^{-1}. The cessation of the decline in alkalinity in 1975 co-incided with fertilization in Middle Lake, an effect comparable to that observed in Hannah Lake. The source of the extra alkalinity is discussed in section I.

I. Nitrate and Ammonium: Generation of ANC by Biological Processes

i. Introduction

It is well known that biologically mediated reactions can affect pH and alkalinity in natural waters (reviewed by Weber and Stumm 1963, Reuss 1975, Harvey et al. 1981). In general, reduction processes raise pH and generate ANC, while oxidation processes lower pH and consume ANC. Two important processes that occur in all aquatic ecosystems are primary production and decomposition:

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \underset{\text{decomposition}}{\overset{\text{production}}{\rightleftarrows}} C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2 \qquad (8\text{-}10)$$

In primary production, the uptake of NO_3^- and HPO_4^{2-} is approximately balanced by the production of OH^- (Brewer and Goldman 1976). However, if NH_4^+ is used as the N source in primary production, uptake is balanced by release of H^+. Since NO_3^- is the prevalent inorganic nitrogen specie in the aerobic euphotic zones of most lakes, primary production is expected to be a net producer of ANC and to raise lake pH (Harvey et al. 1981).

On the other hand, decomposition results in the release of H^+, countering some of the ANC produced by primary production. However, there will be a net increase of ANC resulting from the primary production and decomposition cycle in a lake, because all of the organic material produced is not respired. Some of the material is lost from the lake via the outflow, while some is permanently lost to the lake's sediments (see Chapter 3). As long as these losses cannot be accounted for by allochthonous inputs (ie. by the input of organic material produced in the lake's watershed instead of in the lake itself), a net H^+ consumption must result.

Reduction of sulphate by microbial processes produces alkalinity if the sulphide produced is removed irreversibly from the system:

$$C_{106}H_{263}O_{110}N_{16}P_1 + 53\ SO_4^{2-} \rightarrow 106\ HCO_3- + 53\ H_2S + 16\ NH_3 + H_3PO_4 \qquad (8\text{-}11)$$

Precipitation as FeS is one such mechanism (Schindler et al. 1980).

However, this process is probably only important under anaerobic conditions (eg. in anaerobic hypolimnia or anaerobic lakes under ice cover), although $SO_4{}^{2-}$ reduction may occur in lake sediments.

Reduction of $NO_3{}^-$ (denitrification) by microbial processes may also contribute ANC:

$$5\ C_6H_{12}O_6 + 24\ NO_3^- + 24H^+ \rightarrow 30\ CO_2 + 12\ N_2 + 4\ H_2O \qquad (8\text{-}12)$$

Nitrification, a microbial oxidation process, consumes ANC and decreases pH:

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (8\text{-}13)$$

Of the reactions outlined above, it is expected that primary production and decomposition should have the greatest effect on the acid-base balances of the study lakes. SO_4^{2-} reduction in these lakes can only be important in the sediments, since the lakewaters remained aerobic over the entire course of the study (Chapter 1, Appendix 5).

It was shown in Section H that the measured alkalinities of Hannah and Middle Lakes were substantially greater than those predicted on the basis of an alkalinity mass balance model. In fact, neither lake had been re-acidified by 1979, in contrast to the predictions based on the model. Although there was considerable scatter in the measured values, the major deviations between measured and predicted concentrations began soon after phosphorus additions were initiated. The alkalinity of Lohi Lake, although it has declined to the extent that the lake is now acidic (ie. the pH of the lake is below the alkalinity titration equivalence point), was also greater than the predicted concentration. It has also been shown (Chapter 6, Table 6-10) that the NO_3^- levels of Hannah and Middle Lakes have declined substantially over the course of the study. These changes were attributed to increased primary production resulting from P additions. The NO_3^- level of Lohi Lake over the course of the study has not declined. However, even at steady-state there may have been generation of ANC by primary production. Since NO_3^- is not conservative, a constant generation of ANC may have occurred in all years, without a resulting change in NO_3^- concentration.

There was no consistent difference between measured and predicted alkalinities in Clearwater Lake.

This section evaluates the role of NO_3^- and NH_4^+ uptake as a source of ANC in the study lakes.

ii. Nitrate and Ammonium Mass Balances

a. General Considerations

The seasonal patterns in NO_3^- and NH_4^+ concentration are illustrated for Middle and Hannah Lakes in Fig. 6-3 to 6-6. In Middle Lake, a decrease in NO_3^- concentration (to ~0) each summer, beginning in 1975, was followed by a gradual build-up over the winter to a spring maximum. The NH_4^+ concentration patterns were similar, although the absolute quantities were substantially less.

The net effect of the cycling of the N-species on the ANC production/consumption of the study lakes can be determined on an annual basis by the difference between the uptake of NO_3^- during the growing season and the release during winter, less the uptake of NH_4^+ during the growing season, plus the internal production in the winter. This calculation cannot be done by simply comparing the observed initial and final concentrations of each component for each time interval, since the continued inputs and outputs (via outflow) must be considered. This can be accomplished by using the non-steady state mass balance model to predict the expected concentrations at the end of each time interval and comparing these predictions with the measured concentrations. Since the model accounts for both inputs and loss by outflow, any difference between measured and predicted levels must result from internal processes, ie. uptake (primary production), release (decomposition), or from microbial processes (denitrification, nitrification). However, the latter 2 processes consume or release H^+ in the same proportions as production and decomposition, respectively.

The difference between ANC-producing and ANC-consuming processes cannot be immediately equated to a predicted change in alkalinity, since some of this is also lost by outflow. Instead, these processes can be considered to supply an internal load or input of alkalinity. This "extra" input can be added into the alkalinity mass balance and predictions of expected alkalinity concentration compared to measured levels. In this way, it can be determined if production/decomposition is responsible for the "extra" alkalinity observed.

b. Lohi Lake

Calculations of the net uptake or release of NO_3^- and NH_4^+ in Lohi Lake for the summer and winter periods between June 1977 and December 1979 are outlined in Table 8-27. For example, over the period 77/06-77/08, the NO_3^--N concentration declined from an initial level of 35 mg m^{-3} to 5 mg m^{-3}. However, in the absence of internal uptake or loss mechanisms, the concentration would have reached 51 mg m^{-3}. Therefore, the net uptake of NO_3^--N was 46 mg m^{-3}. Over the same time period, 26 mg NH_4^+-N m^{-3} were also consumed. In the following period (77/08-78/06), an additional 45 mg m^{-3} of NO_3^--N was consumed while 1 mg NH_4^+-N was released. Therefore, the net effect on the ANC of Lohi Lake was a production of 66 mg m^{-3} as N (46 + 45 - (26-1)). This corresponds to an internal load of 11.8 x 10^6 meq (0.59 x 10^9 mg alkalinity).

Comparable calculations can be carried out for all periods over which mass balances were measured (June 1977 - December 1979). However, estimates are needed for ANC production for the period prior to June 1977, because the predictions for the following period require the establishment of the correct initial alkalinity value. To this end, the ANC generation in 1977-1978 was assumed to apply to

Table 8-27. The initial (subscript i), predicted final (subscript pr), and measured final (subscript F) concentrations of NO_3^- and NH_4^+ for 6 time intervals for Lohi Lake. The uptake (positive sign) or release (negative sign) for each component is calculated for each time interval and the net annual change in NO_3^- and NH_4^+ that results in ANC production calculated. All results as mg N m^{-3}.

	77/06/01- 77/08/01	77/08/01- 78/06/01	78/06/01- 78/09/01	78/09/01- 79/05/01	79/05/01- 79/09/01	79/09/01 79/12/31
$[NO_3^--N]_i$	35	5	55	60	90	50
$[NO_3^--N]_{pr}$	51	100	70	122	101	77
$[NO_3^--N]_F$	5	55	60	90	50	70
$[NO_3^--N]_{pr}-[NO_3^--N]_F$	+46	+45	+10	+32	+51	+7
$[NH_4^+-N]_i$	30	10	60	56	35	26
$[NH_4^+-N]_{pr}$	36	59	66	63	48	47
$[NH_4^+-N]_F$	10	60	50	35	26	28
$[NH_4^+-N]_{pr}-[NH_4^+-N]_F$	+26	-1	+16	+28	+22	+19
Net annual effect	+66		+54		+55	

the annual periods from 1975 to 1977.

Calculations of the effects of this additional source of alkalinity on the lake's alkalinity concentration are summarized in Table 8-28. The predicted concentrations at the end of each period were still substantially lower (greater in absolute terms) than the measured levels. For example, the predicted alkalinity concentration at the end of the June 1977 - May 1978 period was $-30\ \mu\text{eq}\ L^{-1}$ based on the measured initial concentration of $-10\ \mu\text{eq}\ L^{-1}$, compared to a measured final value of $-14\ \mu\text{eq}\ L^{-1}$. Therefore, the internal alkalinity generated by the N-cycle can account for only part of the observed extra concentration.

The alkalinity model was also used to determine the input required to yield the observed changes in lake concentration and those inputs compared to the measured inputs (Table 8-28). The calculations for the first period (June 1975 - June 1977) are less precise because the internal alkalinity load generated by the N-cycle was estimated from 1977-1978 data. Furthermore, the external input of alkalinity was not measured, but was calculated from 1973 lake concentrations using steady-state assumptions (section H). The results indicate that, for the two 12-month periods with measured mass balances, the N-cycle contributed ~15% of the alkalinity needed to explain the observed results, while for the period June 1975 - June 1977, it contributed 38%.

c. Hannah Lake

Calculations of the net uptake and/or release of NO_3^- and NH_4^+ in Hannah Lake for 6 time intervals between June 1977 and December 1979 are outlined in Table 8-29. The generation of ANC by these processes was approximately 2-fold greater (on a volumetric basis) than in Lohi Lake ((145 and 84 mg m^{-3} as N (=10.4 and 6.0

Table 8-28. Calculation of the effects of the internal generation of ANC by the N-cycle on the alkalinity concentration of Lohi Lake. J is the external alkalinity load calculated and used in section H; J_I is the additional internal input resulting from the N-cycle; $J_T = J + J_I$; $[TIA]_i$ is the initial alkalinity concentration; $[TIA]_{pr}$ and $[TIA]_f$ are the predicted and measured alkalinity concentrations at the end of the time interval; J_{pr} is the predicted alkalinity input required to yield the measured final alkalinity; J_E is the extra alkalinity input above that supplied by the N-cycle; and $J_I/(J_E+J_I)$ is the proportion of the hypothesized internal input that is supplied by the N-cycle.

Time interval	J	J_I	J_T	$[TIA]_i$	$[TIA]_{pr}$	$[TIA]_f$	J_{pr_9}	J_E	$J_I/(J_E+J_I)$
	10^9 mg yr^{-1}			µeq L^{-1}			10 mg yr^{-1}		%
75/06-77/06	-4.875	0.59[3]	-4.29	80	-18	-10	-3.31	+0.98	38
77/06-78/06	-6.08	0.59	-5.49	-18[1]	-32	-14			
				-10[2]	-30	-14	-2.22	+3.27	15
78/06-79/06	-5.56	0.48	-5.06	-32[1]	-33	-14			
				-14[2]	-27	-14	-2.18	+2.88	14

[1] predicted initial value

[2] measured initial value

[3] assumed equal to the ANC generation in 1977-78

Table 8-29. The initial (subscript i), predicted final (subscript pr), and measured final (subscript F) concentrations of NO_3^- and NH_4^+ for 6 time intervals for Hannah Lake. The uptake (positive sign) or release (negative sign) for each component is calculated for each time interval and the net annual ANC production calculated. All results as mg N m^{-3}.

	77/06/01–77/08/01	77/08/01–78/05/01	78/05/01–78/08/01	78/08/01–79/05/01	79/05/01–79/09/01	79/09/01 79/12/31
$[NO_3^- -N]_i$	260	10	235	<5	150	<5
$[NO_3^- -N]_{pr}$	277	109	271	91	175	56
$[NO_3^- -N]_F$	10	235	<5	150	<5	150
$[NO_3^- -N]_{pr} - [NO\ \ -N]_F$	+267	-126	+271	-59	+175	-94
$[NH_4^+ -N]_i$	60	10	165	20	100	20
$[NH_4^+ -N]_{pr}$	81	90	185	63	114	66
$[NH_4^+ -N]_F$	10	165	20	100	20	16
$[NH_4^+ -N]_{pr} - [NH_4^+ -N]_F$	+71	-75	+165	-37	+94	+50
Net annual effect	+145		+84		+37	

μeq L^{-1} respectively) for Hannah Lake vs 66 and 54 mg m^{-3} as N (=4.7 and 3.9 μeq L^{-1} respectively) for Lohi Lake)) if the period of May 1979 - December 1979 is excluded. The latter period does not include much of the winter, during which additional release of NO_3^- and NH_4^+ are expected.

The greatest declines in NO_3^- concentration in Hannah Lake, however, were observed earlier than 1977 (Fig. 6-3). This might suggest that the ANC generation was greater prior to 1977. However, the input measured in 1977-1978 (1.69×10^8 mg NO_3^--N) was sufficient to maintain a steady-state concentration of 465 mg NO_3^--N m^{-3}.

In order to estimate the contribution of these internal inputs to the differences between the observed and predicted alkalinity concentrations in Hannah Lake, it is necessary to estimate the contribution of the N-cycle for the period following neutralization, but prior to mass balance measurements (June 1975 - May 1977). For the first 12-month period (June 1975 - May 1976), it has been assumed that, since Hannah Lake was not fertilized with P, the contribution of the N-cycle to ANC generation was equal to that in Lohi Lake, which was also unfertilized. In the subsequent 12-month period (June 1976 - May 1977), the ANC generation was assumed equal to that measured in the following 12-month period, since the lake was fertilized in each period.

Calculations of the effects of this additional alkalinity source are summarized in Table 8-30. As was observed in the case of Lohi Lake, the extra alkalinity input contributed by the N-cycle did not account for the observed increases in lake alkalinity. For example, in the period June 1977 - May 1978, the alkalinity of Hannah Lake increased from 64 to 88 μeq L^{-1}. However, a decrease

Table 8-30. Calculation of the effects of the internal generation of ANC by the N-cycle on the alkalinity concentration of Hannah Lake. J is the external alkalinity load calculated and used in section H; J_I is the additional internal input resulting from the N-cycle; $J_T = J + J_I$; $[TIA]_i$ is the initial alkalinity concentration; $[TIA]_{pr}$ and $[TIA]_f$ are the predicted and measured alkalinity concentrations at the end of the time interval; J_{pr} is the predicted alkalinity input required to yield the measured final alkalinity; J_E is the extra alkalinity input above that supplied by the N-cycle; and $J_I/(J_E+J_I)$ is the proportion of the hypothesized internal input that is supplied by the N-cycle.

Time interval	J	J_I	J_T	$[TIA]_i$	$[TIA]_{pr}$	$[TIA]_f$	J_{pr}	J_E	$J_I/(J_E+J_I)$
	—— 10^9 mg yr^{-1} ——			—— μeq L^{-1} ——			— 10^9 mg yr^{-1} —		%
75/06-76/06	-1.09	0.27[1]	-0.82	120	73	73	0.82	0	100
76/06-77/06	-1.09	0.56[2]	-0.53	73	44	64	+0.76	+1.29	30
77/06-78/06	-1.71	0.56	-1.15	44[3]	12	88			
				64[4]	26	88	+2.91	+4.06	12
78/06-79/06	-1.25	0.32	-0.93	12[3]	-6	135			
				88[4]	37	135	+5.92	+6.85	4

[1] assumed ANC generation of 5 μeq L^{-1} (as per Lohi Lake) for this period prior to fertilization.

[2] assumed equal to the ANC generation in 77/06-78/06.

[3] predicted initial value.

[4] measured initial value.

in alkalinity to 26 μeq L^{-1} was expected according to model predictions based on the actual initial alkalinity value. A decrease to 12 μeq L^{-1} was expected, based on the initial value predicted from the previous 12-month period. In fact, the alkalinity input required to yield the observed changes in lake alkalinity was much greater than the N-cycle contributed. This internal input could account for only 12 and 4% of the extra input needed, respectively, indicating that the role of the N-cycle in production/decomposition was not the major reason for the unexpectedly high lake concentrations.

d. Middle Lake

The net uptake and/or release of NO_3^- and NH_4^+ in Middle Lake for 6 time intervals between June 1977 and December 1979 are outlined in Table 8-31. The generation of ANC in Middle Lake was comparable to that in Hannah Lake for the first two 12-month periods, being 129 and 163 mg m^{-3} as N (9.2 and 11.6 μeq L^{-1} respectively). As for Hannah Lake, the third period, beginning in June 1979, was incomplete, precluding calculation of an annual ANC generation.

The contribution of this uptake and release of N-compounds to the alkalinity budget is summarized in Table 8-32. Since mass balances were not measured prior to June 1977, the ANC generation by the N-cycle was estimated for the earlier period from 1977-1978 data. No estimations were made prior to June 1975, because the large scatter in measured lake alkalinity prevented comparison of predicted and measured results for this period. In Middle Lake, the N-cycle contributed between 11 and 46 , respectively, of the ANC required to account for the observed changes in lake alkalinities. As was the case for Lohi and Hannah Lakes, an additional source of

Table 8-31. The initial (subscript i), predicted final (subscript pr), and measured final (subscript F) concentrations of NO_3^- and NH_4^+ for 6 time intervals for Middle Lake. The uptake (positive sign) or release (negative sign) for each component is calculated for each time interval and the net annual ANC production calculated. All results as mg N m^{-3}.

	77/06/01- 77/08/01	77/08/01- 78/05/01	78/05/01- 78/07/01	78/07/01- 79/06/01	79/06/01- 79/10/01	79/10/01 79/12/31
$[NO_3^- -N]_i$	180	10	85	5	90	5
$[NO_3^- -N]_{pr}$	192	109	107	140	107	34
$[NO_3^- -N]_F$	10	85	5	90	5	50
$[NO_3^- -N]_{pr} - [NO\ \ -N]_F$	+182	+24	+102	+50	+102	-16
$[NH_4^+ -N]_i$	10	40	92	20	150	40
$[NH_4^+ -N]_{pr}$	121	88	105	54	149	67
$[NH_4^+ -N]_F$	40	92	20	150	40	74
$[NH_4^+ -N]_{pr} - [NH_4^+ -N]_F$	+81	-4	+85	-96	109	-7
Net annual effect	+129		+163		-16	

Table 8-32. Calculation of the effects of the internal generation of ANC by the N-cycle on the alkalinity concentration of Middle Lake. J is the external alkalinity load calculated and used in section H; J_I is the additional internal input resulting from the N-cycle; $J_T = J + J_I$; $[TIA]_i$ is the initial alkalinity concentration; $[TIA]_{pr}$ and $[TIA]_f$ are the predicted and measured alkalinity concentrations at the end of the time interval; J_{pr} is the predicted alkalinity input required to yield the measured final alkalinity; J_E is the extra alkalinity input above that supplied by the N-cycle; and $J_I/(J_E+J_I)$ is the proportion of the hypothesized internal input that is supplied by the N-cycle.

Time interval	J	J_I	J_T	$[TIA]_i$	$[TIA]_{pr}$	$[TIA]_f$	J_{pr}	J_E	$J_I/(J_E+J_I)$
	10^9 mg yr^{-1}			µeq L^{-1}			10^9 mg yr^{-1}		%
75/06-76/06	-0.45	0.81[3]	0.36	50	32	48	2.18	1.82	31
76/06-77/06	-1.26	0.81[3]	-0.45	32[1]	15	30			
				48[2]	24	30	2.60	2.15	27
77/06-78/06	-0.814	0.81	-0.004	15[1]	9	74			
				30[2]	18	74	6.35	6.35	11
78/06-79/06	1.14	1.02	2.16	9[1]	20	55			
				74[2]	46	55	3.35	1.19	46

[1] predicted initial value

[2] measured initial value

[3] assumed equal to ANC generation in 1977-78

alkalinity must exist.

e. Summary

The uptake and/or release of NO_3^- and NH_4^+ in Lohi, Hannah and Middle Lakes resulted in a net production of alkalinity. However, this alkalinity could account for only 4-46 of that required to explain the observed changes in alkalinity concentration that could not be attributed to the alkalinity mass balances. Since this extra alkalinity must have been generated internally, it may be attributed to the lakes' sediments. It was indicated in Chapter 6 that a major portion of the ANC added during neutralization treatments to Hannah, Middle and, to a lesser degree, Lohi Lake, could not be accounted for by any reactions or chemical changes in the water column. It was also shown that the surficial sediments (~5 cm) of the study lakes which were acidic (pH <5) prior to neutralization, were not acidic after neutralization. Furthermore, the pH of the sediments of Lohi Lake declined again by 1978, following the lake's re-acidification. Although most of these sediment measurements cannot be quantified on a whole-lake basis and, therefore, cannot be directly related to the mass balance approach, the magnitude of the input of alkalinity from the sediments may be comparable to that required to explain the observed results.

J. SO_4^{2-} Mass Balances

i. Clearwater and Lohi Lakes

The SO_4^{2-} concentrations in Clearwater and Lohi Lakes remained constant between 1974 and 1977 (Tables 8-1, 8-2). The slightly higher concentrations measured in 1973 may be a result of the fact that these data were collected over only part of the year, that analytical techniques may have been less precise, or they may reflect a real decrease in SO_4^{2-} concentration resulting from a reduction in input after construction of the 381-m stack by Inco Ltd. in 1972. However, in Clearwater Lake, only 1/2 of the total expected change to a new concentration following a change in input rate would occur within 2-3 years. Therefore, the inputs cannot have changed a great deal as a result of the new stack because the changes in concentration from year to year appear to be insignificant by 1974-1975. The lower SO_4^{2-} concentrations in each lake in 1978 and 1979 may reflect the reduced inputs (relative to the water budgets) that occurred during the shutdown of the smelters in parts of each year (Chapter 2).

In Tables 8-11 and 8-12, the predicted steady-state SO_4^{2-} concentration based on the inputs measured for June 1977 - May 1978 is shown. This is the only 12-month period with measured inputs that did not include any month with shutdown of the smelters These predicted concentrations are lower than the average measured concentrations over the same time period (24.6 mg L^{-1} in Clearwater Lake, 23.9 mg L^{-1} in Lohi Lake) by a substantial amount (26 and 21%, respectively). This indicates either that the SO_4^{2-} inputs are underestimates or that the measured inputs over this time period were substantially lower than the long-term average inputs that would maintain the observed lake concentrations of SO_4^{2-}. The former reason is supported by the fact that the output of SO_4^{2-} from the gauged Clearwater Lake subwatersheds exceeded the input to them as bulk deposition (Chapter 5). Since there is no evidence that the watersheds of Clearwater and Lohi Lakes contain S-bearing minerals, and since there was no significant decline in SO_4^{2-} concentration in these lakes between 1973 and mid-1978, it can be hypothesized that additional S-containing compounds (particularly SO_2) are deposited directly from the atmosphere (Chapter 2). Therefore, the deposition of S-containing compounds (that are oxidized to SO_4^{2-}) directly to the lake surface must be underestimated as well. Since water surfaces are better sinks for SO_2 deposition than are terrestrial surfaces, (Whelpdale and Shaw 1974), the discrepancy between measured and real deposition may be greater for the lakes themselves than for the gauged subwatersheds.

If the total input to Clearwater Lake required to maintain the measured SO_4^{2-} concentrations is calculated, and the contribution from each gauged subwatershed and the estimated contribution from the ungauged portion of the watershed deducted, an estimate of the total input directly to the lake's surface can be obtained and compared to the measured bulk deposition of SO_4^{2-}. The "extra" S input can be calculated using observed lake chemistry in 3 different ways (assuming the "extra" S input is transformed at some stage to SO_4^{2-}). The non steady-state version of the mass balance model (equation 8-3) can be used with the initial and final lake concentrations over each specific time interval (eg. June 1977 - May 1978) to calculate the input required to explain the observed concentrations. Alternately, the average lake concentration can be assumed to be a steady-state value (at least up to May 1978) and the required input calculated (equation 8-3). Finally, the amount of SO_4^{2-} lost via the lake's outflow can be used as a measure of the input since, with no loss by sedimentation, input and output must be equal when the lake concentration is at steady-state.

The first technique has the advantage that the lake does not have to be in steady-state for it to be used. However, small changes in lake concentration over a short time scale can result in relatively large variations in predicted input. For example, the observed initial and final SO_4^{2-} concentrations in Clearwater Lake for the period June 1977 - May 1978 (27.0 and 23.5 mg L^{-1}, respectively) require an input of 21.6 x 10^9 mg. However, the final concentration, 23.5 mg L^{-1}, represented a minor short-term fluctuation in lake chemistry (or an analytical problem), with the levels returning shortly thereafter to ~26-27 mg L^{-1}. With a final concentration of 26.0 mg L^{-1}, the required load would be 39.9 x 10^9 mg (ie. almost 100% greater), while for 27.0 mg L^{-1}, it would be 47.3 x 10^9 mg. Thus, this method is very sensitive to minor variations in lake chemistry, whereas the other 2 techniques are not. Using long-term average lake chemistry to calculate input integrates out short-term variability, but is only applicable during steady-state conditions (ie. not during the shutdown period). Use of the measured output from the lake also eliminates the effects of short-term variability and relies on real measurements rather than model predictions, but, it too, is only applicable during steady-state conditions.

On balance, the latter 2 techniques are the most appropriate for the pre-shutdown period, while the first technique is probably the only acceptable technique for calculations during shutdown.

For Clearwater Lake in the time period June 1977 - May 1978, the measured output of SO_4^{2-} was 42.3 x 10^9 mg, while the predicted steady-state input required to attain the observed mean concentration was very close, 45.9 x 10^9 mg. The average of these numbers, the total predicted SO_4^{2-} load to the lake (44.1×10^9 mg), was 2.7 times the measured bulk deposition on the entire watershed (Table 8-33), while the total excess input above that measured (or extrapolated in the case of the ungauged portion of the watershed), which must have been input to the lake's surface, was 12.0×10^9 mg. The total input directly to the lake's surface (15.0×10^9 mg) must, therefore, have been 4.9 times that measured as bulk deposition, indicating that this additional unmeasured source of SO_4^{2-} is very important and that a major portion of the deposition of S-compounds is not measured by our bulk collectors. Furthermore, the ratio of calculated input to measured bulk deposition was greater for the lake surface (4.9) than for the terrestrial subwatersheds (range of 2.07 - 2.41), indicating that the lake's surface is a more efficient receptor of these additional inputs than is the terrestrial portion of the watershed.

Comparable results were obtained for the June 1978 - May 1979 time period. The subwatersheds exported 2.80 - 3.34 times more SO_4^{2-} than was input as measured bulk deposition, while the total input to the lake was 3.1 times greater than the bulk deposition on the total watershed. These ratios were greater than those measured during the previous period prior to shutdown; however, the latter period includes some time (~ 8 months) during shutdown and some time (~ 4 months) in which the smelters were not shutdown. Furthermore, it is expected that there will be a time lag between deposition of SO_4^{2-} or other substances and their export from watersheds via runoff (Chapter 5). Therefore, no conclusions can be drawn about the effects of shutdown on the SO_4^{2-} mass balances because of the very short time scale covered by the available data. Similarly, no conclusions can be

Table 8-33. Sulphate mass balances for Clearwater Lake and its subwatersheds. The input to the lake surface and each of the terrestrial components by bulk deposition (J_{BD}) was calculated as the area of each receptor multiplied by the bulk deposition rate, and the input to the lake from each receptor (J) was measured. The predicted total input to the lake was calculated using the mass balance model, the predicted input to the lake surface was calculated as the predicted total input to the lake less the measured output from the terrestrial components. The ratio of the measured output from each receptor to the input measured as bulk deposition to the receptor (J/J_{BD}), and the ratio of the predicted input to the measured bulk deposition for the lake surface and the watershed as a whole (J_{pr}/J_{BD}) are given.

Receptor	Input to receptor by bulk deposition (J_{BD})	Input to lake from receptor (J)	Predicted input to lake (J_{pr})	$\frac{J}{J_{BD}}$	$\frac{J_{pr}}{J_{BD}}$
	10^9 mg/time period				
June 1977 - May 1978					
Lake surface	3.04	3.04	15.0		4.9
Subwatershed 1	3.59	7.66		2.13	
Subwatershed 2	1.06	2.56		2.41	
Subwatershed 3	0.88	1.83		2.07	
Subwatershed 4	2.64	5.53		2.09	
Ungauged	5.41	11.5	—	2.13	
Total	16.6	32.1	44.1[1]		2.7
June 1978 - May 1979					
Lake surface	2.33	2.33	5.93		2.6
Subwatershed 1	2.75	9.18		3.34	
Subwatershed 2	0.82	2.63		3.22	
Subwatershed 3	0.68	2.00		2.96	
Subwatershed 4	2.02	5.66		2.80	
Ungauged	4.14	13.8	—	3.33	
Total	12.7	35.6	39.2[2]		3.1
June 1977 - December 1979					
Lake surface	6.90	6.90	21.7		3.1
Subwatershed 1	8.16	21.0		2.57	
Subwatershed 2	2.42	6.68		2.77	
Subwatershed 3	2.00	4.47		2.23	
Subwatershed 4	6.00	13.1		2.18	
Ungauged	12.3	31.6	—	2.57	
Total	37.7	83.7	98.5[3]		2.6

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[1] average of measured output from the lake (42.3×10^9 mg) and predicted steady-state input (45.9×10^9 mg) required to give the observed average concentration

[2] calculated using equation 8-3 and the observed initial (23.5 mg L^{-1}) and final (21.5 mg L^{-1}) concentrations

[3] calculated as measured output from the lake

drawn regarding the effects of shutdown on deposition directly on the lake surface. The ratio of predicted input to input measured as bulk deposition is 2.6, lower than the 4.9 calculated for the earlier time period.

If the entire 31-month time period is used (recognizing that the steady-state conditions may have been briefly upset by shutdown, but assuming that the lag-time for effects minimizes them), the ratio of total predicted input to measured bulk deposition is comparable to that of the individual 12-month time periods, as are the ratios based on the subwatersheds or the lake itself.

Comparable calculations were carried out for Lohi Lake (Table 8-34). On a whole watershed basis, the predicted input was 3.1, 3.7 and 2.9 times the measured bulk deposition to the whole watershed for the June 1977 - May 1978, June 1978 - May 1979, and June 1977 - December 1979 periods, respectively, (ie. the measured deposition of SO_4^{2-} and SO_4^{2-} forming compounds was 27-34% of the total calculated input). The ratios calculated for the lake surface, however, were more variable being 10.9, 3.1 and 6.5, respectively. The ratios based on the terrestrial inputs provide little independent information since both the Clearwater outflow and the ungauged portion of the Lohi Lake watershed, were calculated solely on the basis of Clearwater Lake and watershed data. The ratios calculated on a whole watershed basis were very similar to those obtained for Clearwater Lake.

These results indicated that our bulk deposition measurements accounted for 27-38% (average 33% based on 6 measurements) of the real input of SO_4^{2-} or SO_4^{2-}-producing substances to the entire Clearwater Lake and Lohi Lake watersheds. Our measurements accounted for 30-48% (average of 40%) of these substances deposited

Table 8-34. Sulphate mass balances for Lohi Lake and its subwatersheds. The input to the lake surface and each of the terrestrial components by bulk deposition (J_{BD}) was calculated as the area of each receptor multiplied by the bulk deposition rate, and the input to the lake from each receptor (J) was measured. The predicted total input to the lake was calculated using the mass balance model, the predicted input to the lake surface was calculated as the predicted total input to the lake less the measured output from the terrestrial components. The ratio of the measured output from each receptor to the input measured as bulk deposition to the receptor (J/J_{BD}), and the ratio of the predicted input to the measured bulk deposition for the lake surface and the watershed as a whole (J_{pr}/J_{BD}) are given.

Receptor	Input to receptor by bulk deposition (J_{BD})	Input to lake from receptor (J)	Predicted input to lake (J_{pr})	$\frac{J}{J_{BD}}$	$\frac{J_{pr}}{J_{BD}}$
	10^9 mg/time period				
June 1977 - May 1978					
Lake surface	1.61	1.61	17.6		10.9
Clearwater outflow	16.6	42.3		2.55	
Ungauged	3.91	8.32		2.13	
Total	22.2	52.2	68.2[1]		3.1
June 1978 - May 1979					
Lake surface	1.23	1.23	3.83		3.1
Clearwater outflow	12.7	48.7		3.83	
Ungauged	3.00	9.99		3.33	
Total	16.9	59.9	62.5[2]		3.7
June 1977 - December 1979					
Lake surface	3.65	3.65	23.65		6.5
Clearwater outflow	37.7	98.5		2.61	
Ungauged	8.87	22.8		2.57	
Total	50.3	125.	145.[3]		2.9

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[1] average of measured output from the lake (67.1×10^9 mg) and predicted steady-state input (69.2×10^9 mg) required to give the observed average concentration

[2] calculated using equation 8-3 and the observed initial (21.5 mg L^{-1}) and final (20.5 mg L^{-1}) concentrations

on the terrestrial portion of the watersheds, but only 9-38% (average 24%) of that deposited on the lakes' surfaces. Because the calculation of the input directly to the lakes' surfaces is done by difference between total predicted input and total measured input, the results are less reliable than those for the terrestrial portions of the watersheds or those based on the whole watersheds. For example, a 10% reduction in predicted total input to Clearwater Lake in June 1977 - May 1978 (ie. 10% of 44.1 x 10^9 mg) would result in a change in the input to the lake surface from 15.0 x 10^9 mg to 10.6 x 10^9 mg. The ratio of predicted input to measured input would, therefore, be reduced from 4.9 to 3.5 for the lake surface, but only from 2.7 to 2.4 for the whole watershed. Nevertheless, these results indicate that the lake surfaces are at least as efficient as the terrestrial watersheds in scavenging SO_4^{2-} or SO_4^{2-}-producing substances.

ii. Middle and Hannah Lakes

The SO_4^{2-} concentrations in Hannah and Middle Lakes did not change very much between 1974 and 1977 (Tables 8-3, 8-4). Slightly higher concentrations in Middle Lake in 1973 compared to the other years may have resulted for the same reasons as postulated for the similar finding for Lohi and Clearwater Lakes, while the lower concentrations in 1978-1979 may reflect the decreased deposition during the shutdown of the smelters (Chapter 2).

In Tables 8-13 and 8-14, the predicted steady-state concentrations for Hannah and Middle Lakes, respectively, are shown. These are based on the measured inputs over 5 (overlapping) time periods. In June 1977 - May 1978, the period unaffected by shutdown of the smelters, the measured concentrations for Hannah and Middle Lakes were 165 and 11% greater, respectively, than predicted on the basis of the steady-state model, indicating that an additional major input to Hannah Lake occurs. In the case of Middle Lake, the difference is much smaller because a major portion of the total input is the Hannah Lake outflow (which is measured). This input has excess (unmeasured) deposition to the Hannah Lake watershed included in it. For the same reasons as discussed for Clearwater and Lohi Lakes, it is apparent that our bulk deposition measurements underestimated the input of SO_4^{2-} or SO_4^{-2}-producing water compounds, and that dry deposition of SO_2 is the most likely additional input. Calculations based on measured lake SO_4^{2-} concentrations can again be used to estimate total deposition. However, the separation of additional deposition on the lake surface and on the terrestrial watersheds for these lakes may be inaccurate, because the "measured" input from the terrestrial sources is an extrapolation of data collected for the Clearwater Lake watersheds. These watersheds, which are more distant from Copper Cliff, may receive a lesser input of SO_2, as suggested in Table 2-23, which is reflected in Clearwater and Lohi Lake SO_4^{2-} concentrations being only half those of Hannah and Middle Lakes.

For Hannah Lake, the required total deposition of SO_4^{2-} and SO_4^{2-}-producing compounds was 4.4, 4.3 and 4.2 times the measured bulk deposition on the entire watershed (including the lake surface) for the 1977-1978, 1978-1979 and 1977-1979 time periods, respectively (Table 8-35). These ratios are ~50% greater than those obtained for Clearwater and Lohi Lakes, indicating that the unmeasured additional input is a greater proportion of the total input to Hannah Lake. In fact, the measured bulk deposition accounts for an average of only ~23% of the calculated total input to the Hannah Lake watershed. Separation of the excess into that

Table 8-35. Sulphate mass balances for Hannah Lake and its subwatersheds. The input to the lake surface and each of the terrestrial components by bulk deposition (J_{BD}) was calculated as the area of each receptor multiplied by the bulk deposition rate, and the input to the lake from each receptor (J) was measured. The predicted total input to the lake was calculated using the mass balance model, the predicted input to the lake surface was calculated as the predicted total input to the lake less the measured output from the terrestrial components. The ratio of the measured output from each receptor to the input measured as bulk deposition to the receptor (J/J_{BD}), and the ratio of the predicted input to the measured bulk deposition for the lake surface and the watershed as a whole (J_{pr}/J_{BD}) are given.

Receptor	Input to receptor by bulk deposition (J_{BD})	Input to lake from receptor (J)	Predicted input to lake (J_{pr})	$\frac{J}{J_{BD}}$	$\frac{J_{pr}}{J_{BD}}$
	10^9 mg/time period				
June 1977 - May 1978					
Lake surface	1.23	1.23	14.0		11.4
Ungauged	3.44	6.45		1.9	
Total	4.67	7.69	20.5[1]		4.4
June 1978 - May 1979					
Lake surface	0.99	0.99	9.35		9.4
Ungauged	2.78	7.74			
Total	3.77	8.74	16.1[2]		4.3
June 1977 - December 1979					
Lake surface	2.81	2.81	26.9		9.6
Ungauged	7.84	17.7		2.3	
Total	10.6	20.5	44.6[3]		4.2

[1] average of measured output from the lake (20.0×10^9 mg) and predicted steady-state input (20.9×10^9 mg) required to give the observed average concentration

[2] calculated using equation 8.3 and the observed initial (50.0 mg L^{-1}) and final (47.8 mg L^{-1}) concentrations

[3] calculated as measured output from the lake

deposited on the lake surface and that deposited on the terrestrial portion of the watershed suggests that the lake ratio is very high (9.4 - 11.4), while the terrestrial ratio is low (1.9 - 2.8); however, the differences between the two are probably greatly accentuated by using export data from Clearwater Lake watershed 1 to estimate the contribution to Hannah Lake from its ungauged area. The real input of SO_4^{2-} from the Hannah Lake ungauged area is certainly greater, meaning the terrestrial ratios are underestimates and the lake surface ratios are overestimates.

Alternate calculations can be done using data for Middle Lake watershed 1, instead of Clearwater Lake watershed 1, to estimate the contribution from the ungauged Hannah Lake watershed. These data, although incomplete relative to those for Clearwater Lake watershed 1, are more representative of the Hannah and Middle Lake watersheds (Chapter 5). If this is done, the ratios of actual input on the lake's surface and measured input drop to 6.9, 4.7 and 6.1 for June 1977 - May 1978, June 1978 - May 1979 and June 1977 - December 1979, respectively, while the corresponding terrestrial ratios are 3.5, 4.1 and 3.5, respectively.

The Middle Lake results (Table 8-36) are intermediate between those of Hannah Lake and those of Clearwater and Lohi Lakes. The ratio of predicted total input to the lake, to measured bulk deposition on the entire watershed ranged from 2.9 to 4.9, indicating that our collectors measured 20-34% of the SO_4^{2-} and SO_4^{2-}-producing substances. The ratios for the lake surface (2.8 - 10.5) were generally greater than those for the terrestrial portion of the watershed (3.5 - 4.2 for subwatershed 1). However, since these calculations rely, in part, on measurements for Clearwater watershed 1, they overestimate the lake ratio and

Table 8-36. Sulphate mass balances for Middle Lake and its subwatersheds. The input to the lake surface and each of the terrestrial components by bulk deposition (J_{BD}) was calculated as the area of each receptor multiplied by the bulk deposition rate, and the input to the lake from each receptor (J) was measured. The predicted total input to the lake was calculated using the mass balance model, the predicted input to the lake surface was calculated as the predicted total input to the lake less the measured output from the terrestrial components. The ratio of the measured output from each receptor to the input measured as bulk deposition to the receptor (J/J_{BD}), and the ratio of the predicted input to the measured bulk deposition for the lake surface and the watershed as a whole (J_{pr}/J_{BD}) are given.

Receptor	Input to receptor by bulk deposition (J_{BD})	Input to lake from receptor (J)	Predicted input to lake (J_{pr})	$\frac{J}{J_{BD}}$	$\frac{J_{pr}}{J_{BD}}$
	10^9 mg/time period				
June 1977 - May 1978					
Lake surface	1.27	1.27	3.57		2.8
Hannah outflow	4.67	20.0		4.3	
Subwatershed 1	0.16	0.57		3.5	
Ungauged	6.28	11.8		1.9	
Total	12.4	33.6	35.9[1]		2.9
June 1978 - May 1979					
Lake surface	1.03	1.03	10.8		10.5
Hannah outflow	3.77	23.1		6.1	
Subwatershed 1	0.13	0.54		4.2	
Ungauged	5.07	14.1		2.8	
Total	10.0	38.8	48.6[2]		4.9
June 1977 - December 1979					
Lake surface	2.90	2.90	15.8		5.4
Hannah outflow	10.7	44.6		4.2	
Subwatershed 1	0.37	1.30		3.5	
Ungauged	14.3	32.3		2.3	
Total	28.3	81.1	94.0[3]		3.3

[1] average of measured output from the lake (35.0 x 10^9 mg) and predicted steady-state input (36.8 x 10^9 mg) required to give the observed average concentration

[2] calculated using equation 8-3 and the observed initial (37.8 mg L^{-1}) and final (33.5 mg L^{-1}) concentrations

[3] calculated as measured output from the lake

underestimate the terrestrial ratio.

In summary, the deposition of SO_2 and other SO_4^{2-}-producing substances, in excess of that measured as bulk deposition, is the major SO_4^{2-} source for Hannah and Middle Lakes, providing ~66-80% of the total SO_4^{2-} input. The input of strong acids is, therefore, underestimated by a comparable amount.

K. The Net Export of Cations: Calculation of the Dry Deposition of Strong Acids

i. Introduction

In Chapter 5, it was shown that, for each of the watersheds studied (4 at Clearwater Lake, 1 at Middle Lake, 6 at Nelson Lake), there was a substantial net export of SO_4^{2-} (Tables 5-10, 5-11); that is, the gross output of SO_4^{2-} was greater than the input measured as bulk deposition. It was also shown (Table 5-18) that the amount of bases exported from the watersheds (or acids consumed in the watersheds) was much greater than the acids supplied to the watersheds, measured as bulk deposition. It was hypothesized that a significant input of SO_2 was not included in the measured bulk deposition. This was supported by the fact that the net export of SO_4^{2-} closely balanced the deficiency in input of strong acids (Table 5-19), suggesting that, following deposition, the SO_2 was oxidized and hydrolyzed, yielding H_2SO_4.

In section J of this chapter, it was also shown that the SO_4^{2-} concentrations measured in the study lakes were higher (at steady-state) than could be supported by the measured input rates. There are several possible explanations for this observation. The watersheds could contain S-bearing minerals, resulting in greater input to the lakes from their ungauged areas than estimated based on measurements at the Clearwater Lake watershed 1. However, there is no field evidence that such minerals exist in these watersheds (Appendix 2c) and the S content of the quartzite and metagabbro bedrock is the lowest of all the rock types in the Sudbury area (Table A2c-4, Appendix 2c). Subsequent calculations (Tables 8-32 to 8-36) indicated that deposition of SO_4^{2-} or SO_4^{2-}-producing substances directly to the lakes' surfaces was an important input to these lakes.

In this section, a fourth method of using the mass balances to estimate the dry deposition of strong acid or strong-acid producing substances is outlined. Results obtained using all methodologies are compared.

ii. The Net Export of Cations to Hannah and Middle Lakes

Although the Mg^{2+} and K^+ concentrations in Hannah and Middle Lakes appear to be at steady-state levels (Tables 8-3, 8-4), these levels are well in excess of those predicted from the best estimates of the inputs to these lakes. These estimates are based partially on measurements (bulk deposition on the lakes' surfaces, Hannah Lake's outflow to Middle Lake), but largely on extrapolations from other measured mass balances (the inputs from the ungauged areas are approximated from Clearwater Lake watershed 1). Although the Na^+ and Ca^{2+} levels are not presently in steady-state because of the additions of NaCl, $CaCl_2$ and neutralizing agents ($CaCO_3$, $Ca(OH)_2$), they were in steady-state in 1973-1974 before any of these additional impacts occurred. These levels were also greater than the levels that the current estimated inputs can support. There is no reason to believe that major increases in the inputs of Ca^{2+} and Na^+ have occurred over the course of the study, other than as a result of these recent extra impacts. Therefore, it can be assumed that the portion of the inputs attributable to loss (ie. weathering) from the ungauged areas has been underestimated.

If it is assumed that the extra Ca^{2+}, Mg^{2+}, Na^+ and K^+ in Hannah Lake result from unmeasured deposition of strong acids or acidifying substances, followed by leaching and export, then the extra input required to reach observed lake steady-state levels can be calculated and the corrected weathering rates obtained. To do this, the lake concentrations measured in 1977-1979 have been used for Mg^{2+} and K^+, while the concentrations measured in 1973, prior to neutralization or $NaCl/CaCl_2$ road treatments have been used for Na^+ and Ca^{2+}. The calculated inputs for Hannah Lake are shown in Table 8-37. Inputs to the lake surface from bulk deposition (Chapter 2) are subtracted from predicted inputs required to maintain measured lake levels, to give the total predicted terrestrial input. This is converted to export on an areal basis.

The total net export of major cations ($\Sigma M = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) from the Hannah Lake watershed, as calculated in this manner, varied from 508 to 757 meq m^{-2} yr^{-1} and was 1290 meq m^{-2} over the 31-month period of the mass balance study. These figures are underestimates of the total acid consumed in the watershed, since other reactions also provide bases and/or consume acids. The export of Al^{3+} and the consumption of NO_3^- also affect the acid-base balance of the watershed. Because these are not conservative substances, their net export cannot be calculated from lake concentrations as was done for the major cations. However, estimates based on measurements made for Middle Lake

Table 8-37. Calculation of net export rates for the Hannah Lake watershed using mass balance models. The "measured" input (J_M) was estimated from Clearwater Lake watershed 1 and bulk deposition on the lake surface, the predicted input (J_{pr}) was calculated from lake chemistry (1973-74 concentrations for Na^+ and Ca^{2+} - see text), and the terrestrial input (J_{TR}) is J_{pr}-input by bulk deposition to the lake surface (all inputs in 10^9 mg per time period). The gross and net (gross-input by bulk deposition) export (in meq m^{-2} per time period) are calculated.

	June 1977-May 1978	June 1978-May 1979	June 1977-Dec. 1979
Mg^{2+}			
J_M	0.39	0.43	1.02
J_{pr}	1.89	2.17	4.19
J_{TR}	1.86	2.15	4.13
gross export	201	232	446
bulk deposition	8.1	6.6	18
net export	193	225	428
K^+			
J_M	0.22	0.26	0.50
J_{pr}	0.82	1.08	1.97
J_{TR}	0.79	1.06	1.90
gross export	26	34.8	62.4
bulk deposition	3.1	2.4	6.5
net export	22.9	32.4	55.9
Na^+			
J_M	0.75	0.71	1.65
J_{pr}	1.39	1.97	3.46
J_{TR}	1.11	1.79	2.98
gross export	63.0	101.8	169
bulk deposition	45.3	28.1	76.5
net export	17.7	73.7	92.6
Ca^{2+}			
J_M	1.61	1.81	4.26
J_{pr}	5.04	7.15	12.6
J_{TR}	4.82	6.98	12.1
gross export	315	456	794
bulk deposition	41.1	30.7	83.4
net export	274	426	710
$\Sigma(Ca^{2+} + Na^+ + K^+ + Mg^{2+})$		508	757 1290

watershed 1 indicate that 24.7, 26.4 and 52.5 meq Al^{3+} m^{-2} and 35.3, 37.8 and 92.9 meq NO_3^- m^{-2} may be contributed to the acid-base balance for June 1977 - May 1978, June 1978 - May 1979 and June 1977 - December 1979, respectively. The total amount of acid consumed over the same 3 time periods was, therefore, 568, 821 and 1435 meq m^{-2}, respectively. These figures are much higher than those based on estimation of the inputs by extrapolation of the Clearwater Lake watershed data. This result again indicates that a major input of strong acid to the Hannah Lake watershed, in excess of that measured as bulk deposition, has occurred.

A comparable calculation can be done for Middle Lake (Table 8-38). However, it is expected to be less precise because the measured input from the Hannah Lake outflow, from Middle Lake watershed 1 and from bulk deposition directly on Middle Lake must be subtracted from the predicted input to estimate the input from the ungauged area. This estimate is, therefore, a smaller proportion of the predicted total input and is thus subject to proportionately greater errors.

To carry out this calculation, the effects of $NaCl/CaCl_2$ treatments on these inputs must be considered. First, the Hannah Lake outflow supplied some of the Na^+ and Ca^{2+}, distributed in the Hannah Lake watershed, to Middle Lake and correction for this extra Na^+ and Ca^{2+} input must be made. To do this, it can be assumed that the input of these elements to Hannah Lake in 1973 and 1974, prior to any treatments (road applications or neutralization), as calculated from the steady-state model, is equal to the output from the lake, and that this output has remained constant over the course of the study. Second, excess Cl^- export from Middle Lake subwatershed 1 is also evident (Chapter 5), indicating road

Table 8-38. Calculation of net export rates for the Middle Lake watershed using mass balance models. The "measured" input (J_M) includes bulk deposition on the lake surface, the Hannah Lake outflow, Middle Lake watershed 1 and the contribution from the ungauged portion of the watershed extrapolated from Clearwater Lake watershed 1. The predicted input (J_{pr}) was calculated from lake chemistry (1973 concentrations for Na^+ and Ca^{2+} - see text) and the terrestrial input (J_{TR}) is J_{pr} - (input by bulk deposition to the lake surface + the Hannah Lake output + input from Middle Lake watershed 1) (all inputs in 10^9 mg per time period). The gross and net (gross-input by bulk deposition) export (meq m^{-2} per time period) are calculated.

	June 1977- May 1978	June 1978- May 1979	June 1977- Dec. 1979
Mg^{2+}			
J_M	2.62	2.98	6.10
J_{pr}	3.23	4.82	8.54
J_{TR}	1.27	2.59	4.19
gross export	75	153	248
bulk deposition	8.1	6.6	18
net export	67	146	230
K^+			
J_M	1.21	1.55	2.87
J_{pr}	1.45	2.44	4.15
J_{TR}	0.58	1.32	2.07
gross export	10.4	23.8	37.3
bulk deposition	3.1	2.4	6.5
net export	7.3	21.1	30.8
Na^+			
J_M	10.3	14.4	26.0
J_{pr}	2.23	3.82	6.41
J_{TR}	0.51	1.63	2.36
gross export	15.9	50.7	73.4
bulk deposition	45.3	28.1	76.5
net export	-29.4	22.6	-3.1
Ca^{2+}			
J_M	10.1	11.6	23.7
J_{pr}	9.1	15.6	26.2
J_{TR}	3.70	8.17	12.9
gross export	132.6	292.7	462.2
bulk deposition	41.1	30.7	83.4
net export	91.5	262	379
$\Sigma(Ca^{2+} + Na^+ + K^+ + Mg^{2+})$	136	452	637

applications of neutral salts. Export of Ca^{2+} was corrected by subtracting the measured net Cl^- export since net export of Cl^- is expected to be ~0 where no Cl-bearing minerals occur (Chapter 5). Na^+ export was not elevated, indicating that the excess export could be attached entirely to Ca^{2+}.

The calculated net exports for the ungauged portion of the Middle Lake watershed (Table 8-38) are, as for Hannah Lake, much greater than the estimates derived from the Clearwater Lake watershed data, at least for 2 of the 3 time periods considered.

The predicted net export rates for the ungauged Middle Lake watershed should be similar to the measured export rates for the Middle Lake watershed 1, because of their proximity and uniformity of the geology (Appendix 2c). Net export rates for the 3 periods are compared in Table 8-39. The predicted total net export of cations (637 meq m^{-2}) was only 9% greater than that measured for watershed 1 for the 31-month period (582 meq m^{-2}). The differences were much greater for the 12-month periods; this is at least partly expected, since short-term changes in export rates will not be immediately reflected in the lake chemistry which was used to calculate predicted input rates.

iii. Excess Acid Deposition: Comparison of Methods

The net export rates of the major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) that were estimated in the previous subsection can be combined with the NO_3^- consumed and Al^{3+} exported (measured for Middle Lake watershed 1) to give a measure of the net acid consumed in the Hannah and Middle Lake watersheds. Since the net acid consumed must equal the net acid supplied (Chapter 5), the difference between calculated acid consumed and acid supplied represents the unmeasured input of acid. The results calculated in

Table 8-39. Comparison of the net export rates of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} between Middle Lake watershed 1 (measured results) and the ungauged portion of the Middle Lake watershed (predicted on the basis of the mass balance modelling). All results in meq m^{-2} per time period.

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Total
June 1977–May 1978					
watershed 1	141	88.6	3.0	7.6	240
ungauged	91.5	67.0	-29.4	7.3	136
June 1978–May 1979					
watershed 1	141	79.9	16.2	7.6	245
ungauged	262	146	22.6	21.1	452
June 1977–December 1979					
watershed 1	332	198	32.9	17.8	582
ungauged	379	230	-3.1	30.8	637

this way can be compared to the previous estimates of extra acid input (Chapter 5) that were based on net SO_4^{2-} export from the watersheds or the difference between measured acid consumed by and acid supplied to the watersheds.

Another independent calculation of the extra acid supplied to the watersheds can be obtained from section J, using the calculated extra SO_4^{2-} input to the lakes. This extra SO_4^{2-} input can be equated to the unmeasured deposition of acid-producing substances, principally SO_2.

Results for the Middle Lake watershed are summarized in Table 8-40. The measured net acid supply ($H^+ + NH_4^+ + H_2CO_3$) for June 1977 - December 1979 was 207 meq m^{-2}. The measured consumption of acid (ie. the net export of $Ca^{2+} + Mg^{2+} + K^+ + Na^+ + Al^{3+}$ + retention of NO_3^-), however, was much higher, being 727 meq m^{-2} in Middle Lake watershed 1. This result compares very favourably with the acid consumption (782 meq m^{-2}) calculated for the ungauged area of the watershed using the lake's major ion budgets (Ca^{2+}, Mg^{2+}, Na^+, K^+). Al^{3+} export and NO_3^- retention measured for watershed 1 were included in this calculation. Clearly, the net acid consumption was much greater than the measured supply. If the supply is corrected by adding either the net SO_4^{2-} export from watershed 1 or the extra SO_4^{2-} exports calculated from the lake's SO_4^{2-} mass balance, then the total calculated net acid supply (743 and 628 meq m^{-2}, respectively) is in very good agreement with the net acid consumption, again affirming that a major input of S-associated strong acid is not included in the bulk deposition.

Calculations on a 12-month basis gave results that were qualitatively similar. However, the agreement between the different

Table 8-40. Calculation of the net acid consumption and net acid supply for the Middle Lake watershed.

	Source of data	June 1977-May 1978	June 1978-May 1979	June 1977-Dec. 1979
Net Acid Supply				
-measured for Middle Lake watershed 1	Table 7-14	92.1	72.1	207
Net Acid Consumption				
-measured for Middle Lake watershed 1	Table 7-14	300	309	727
-calculated for the ungauged area by major ion budgets	Tables 8-38, 7-11, 7-12, 7-13	196	516	782
Total Net Acid Supply				
-measured net acid supply + net SO_4^{2-} export for watershed 1	Table 7-14	327	310	743
-measured net acid supply + extra SO_4^{2-} export calculated from lake budgets	Table 8-35	204	320	628

methods for assessing the extra acid supplied was poorer than achieved over the longer time period. This is undoubtedly a result of the fact that 2 methods were based on lake chemistry (SO_4^{2-} lake mass balance method, major ion lake mass balance method), while 2 were based on watershed mass balances (SO_4^{2-} export method and measured net acid consumption method). The lake chemistry can not rapidly reflect changes in watershed mass balances. Instead, changes in the watershed's export rates will only slowly affect the lake chemistry, which, therefore, integrates out short-term variability.

The contribution of unmeasured deposition to the total supply of strong acid by SO_4^{2-}-producing substances is shown in Table 8-41. Since this unmeasured input both supplies strong acid and produces SO_4^{2-}, it can be concluded that this substance is SO_2. The calculations, carried out using 4 independent methods are remarkably consistent. They indicate that, over the 31-month period, 71% of the input of strong acid was not collected as part of our bulk deposition measurements, with the range being only 67-74% for the 4 different techniques. During the 12-month periods (June 1977 - May 1978, June 1978 - May 1979), these calculations indicated that averages of 63 and 79% of the strong acid input was unmeasured. As discussed earlier, the response time of both the lake and its watershed to a change in input rate is too slow to interpret these results in terms of any impact resulting from the shutdown of the smelters in 1978-79.

Calculation of the extra input of strong acid to Hannah Lake can be done using only the methods based on lake SO_4^{2-} concentrations and lake major ion concentrations since there were no gauged watersheds. The resulting calculations of net acid supply

Table 8-41. Contribution of the unmeasured input of strong acid or acid-producing substances to the total acid supply to the Middle Lake watershed (in %).

Method of calculation	June 1977-May 1978	June 1978-May 1979	June 1977-Dec. 1979
Net acid consumption - net acid supply (Middle Lake watershed 1)	69	77	72
Net acid consumption (by major ion balances) -net acid supply	53	86	74
Net SO_4^{2-} export (Middle Lake watershed 1)	72	77	72
Lake SO_4^{2-} mass balances	55	77	67
Mean	62	79	71

(435, 340, 946 meq m^{-2} for June 1977 - May 1978, June 1978 - May 1979, June 1977 - December 1979, respectively) and net acid consumption (568, 821, and 1435 meq m^{-2} for the same time periods) are a) substantially greater than those calculated for Middle Lake, and b) not in as good agreement with each other as the Middle lake results. These results indicate that, at Hannah Lake, 78-92% of the deposition of strong acids was unmeasured.

Although Hannah Lake is close to Middle Lake, other evidence supports the finding that it receives a greater deposition. The SO_4^{2-} concentration in the lake (Table 8-3) was ~30% greater than in Middle Lake (Table 8-4) in 1973-74 before any manipulation of the lakes, whereas the concentrations in Lohi and Clearwater were almost identical.

The same phenomenon is apparent for Cu and Ni (Appendix 6), two other substances that are emitted in substantial quantities by the smelters. The Cu and Ni concentrations of Lohi and Clearwater Lake (before any manipulations of the lakes) were very similar, however, the concentrations in Hannah Lake were substantially greater than those in Middle Lake. These differences may be a result of an exponential decrease in deposition rate of large particulate material emitted from the stack at Copper Cliff or of a similar effect resulting from a dominant effect of low altitude (fugitive) emissions.

iv. Summary

The strong acid supplied to the Middle Lake watershed in excess of that measured as bulk deposition has been estimated by 4 methods. The results obtained are extremely consistent and indicate that 70% of the total input was unmeasured. Since this extra input of acid produces SO_4^{2-}, it is undoubtedly SO_2. Because some dry deposition may be collected by the bulk samplers, this figure is a minimum estimate of the dry deposition of SO_2. At Hannah Lake, the contribution is probably between 80 and 90%.

A summary of the results based on all methods of calculation (acid supply-acid consumption (Chapter 5), net SO_4^{2-} export (Chapter 5), lake SO_4^{2-} budgets, and the major ion balances) is shown in Table 8-42. The proportion of the input of SO_4^{2-} - precursors/strong acid which was not measured by bulk deposition collectors calculated on the basis of the 4 independent methodologies was remarkably consistent for each site. For example, at Middle Lake, where all 4 methodologies were used, the predicted unmeasured input ranged from only 70 to 73% of the calculated total input. Nelson Lake had the broadest range (50-61%) but even these results were remarkably consistent.

The importance of the unmeasured inputs decreased with distance from Copper Cliff, the unmeasured fraction averaging 81, 72, 66, 59 and 57% of the total input at Hannah, Middle, Lohi, Clearwater and Nelson Lakes respectively. This provides additional evidence that Copper Cliff is the source of the SO_2.

This "extra" or unmeasured input of strong acid has not been completely taken into account in the lakes' alkalinity (or acidity) mass balances. The additional input to each lake's watershed is, of course, included in the measured or extrapolated inputs from the terrestrial watershed, but the additional direct input to the lake's surfaces has not been considered. The total input of strong acid to the lakes is therefore greater than indicated in section H, but the magnitude of the difference is not known accurately enough to warrant recalculation.

Table 8-42 Proportion (%) of the input of SO_4^{2-} precursors or acid not measured by bulk deposition.

Method	Clearwater	Lohi	Hannah	Middle	Nelson
Watershed SO_4^{2-} budgets	59	-	-	72	61
Lake SO_4^{2-} budgets	62	66	76	70	60
Acid input-Acid consumed	56	-	-	72	50
Lake ion budgets	-	-	86	73	-

L. Trace Metals

i. Introduction

In previous chapters, it has been shown that, in the Sudbury area, the concentrations of metals in the lakes (both in the water (Chapter 1) and in the sediments (Chapter 3), in streams (Chapter 5), and in wet and bulk deposition (Chapter 2) were much greater than in any other regions of Ontario. In fact, in many cases, concentrations were greater than any reported elsewhere in the world (eg. for bulk deposition of Ni).

It has also been shown that the metal concentrations (particularly Cu) in Middle Lake after neutralization, even though much reduced relative to those measured prior to neutralization, were too high to permit the lake to support a fish population (Chapter 6). Therefore, where initial metal concentrations are high, successful restoration of the study lakes will require a reduction in metal concentration in excess of that resulting from neutralization.

The source of these metals in the study lakes is the deposition from the atmosphere of material emitted by the smelters and associated operations, particularly at Copper Cliff, or the deposition and subsequent interactions of strong acids with the lakes' watersheds. This was demonstrated by the sediment chronologies (Chapter 3) and by the observations made during the shutdown of the smelters (Chapter 2). Bulk deposition of Cu and Ni decreased by up to 2 orders of magnitude during shutdown to levels which were not statistically different from those in Muskoka-Haliburton (Scheider _et_ _al_., 1981).

The purpose of this section is to estimate the reduction in inputs of metals to the study lakes that are required to yield lake and stream concentrations that are suitable for re-establishment of typical Precambrian biotic communities. Because the deposition of metals (Cu, Ni, Fe, Zn) was affected by the shutdown (Chapter 2) and because the total inputs to the study lakes (Cu, Zn, possibly Ni) were significantly lower during shutdown than before shutdown (Chapter 8, section C), the mass balance data collected prior to shutdown are the only data suitable for assessing this question.

Variations in watershed retention coefficients (Chapter 5) were observed for Cu, Ni, and Zn in response to the reduced atmospheric deposition during shutdown. Those results suggest that a lag-time should be expected between reduction in inputs and the corresponding reduction in watershed export. The length of this period during which metals previously accumulated in the watersheds continue to be washed out is unknown, but recovery of the lakes will be delayed until this process is virtually complete.

ii. Metal Concentrations

The inputs and outputs of Cu, Ni, Zn, Fe, Mn and Al to the 5 major study lakes are summarized in Table 8-43 for June 1977-May 1978. From these data, several generalizations can be made.

First, in the acidic lakes (Clearwater and Lohi Lakes), Cu and Ni behaved like conservative substances; that is, they were removed from the lakes only via outflow. Their expected concentrations can, therefore, be predicted by use of the mass balance model used for other conservative substances.

Second, some of the Zn and much of the Fe inputs were retained in both Clearwater and Lohi Lakes. In Lohi Lake, some of the Mn and Al was also retained, while, in Clearwater Lake, little if any Al was retained and more Mn was lost from the lake via outflow than was input. These findings are consistent with those

Table 8-43. Input and output of trace metals to the study lakes for June 1977-May 1978. all figures in 10^8 mg yr^{-1}. Figures in brackets are calculated on the basis of Middle Lake watershed 1 data instead of Clearwater Lake watershed 1 data.

		Clearwater	Lohi	Hannah	Middle	Nelson
Cu	input	1.41	2.08	0.97 (1.69)	1.66 (2.97)	1.65
	output	1.52	1.74	0.49	0.84	0.36
Ni	input	4.71	6.23	1.16 (3.39)	3.72 (7.77)	1.10
	output	4.79	6.50	1.69	4.05	0.35
Zn	input	1.14	1.12	0.22 (0.32)	0.41 (0.58)	2.48
	output	0.73	0.88	0.10	0.32	0.22
Fe	input	14.2	6.56	3.36 (2.44)	5.97 (4.30)	15.0
	output	2.78	3.12	0.66	1.60	2.30
Mn	input	3.20	7.87	0.71 (0.82)	1.75 (1.95)	3.68
	output	4.93	6.17	0.44	1.85	0.99
Al	input	7.36	8.38	1.32 (2.24)	2.99 (4.67)	11.7
	output	6.70	4.56	0.60	1.05	1.61

reported for artificially acidified waters (Hesslein et al. 1980). In addition, these findings provide an explanation for one aspect of the observed sediment chemistry of the study lakes (Chapter 3). The decrease in metal content in the sediments deposited within the most recent 1-3 decades relative to older sediments may be explained by the low retention of some metals by the lakes when they are acidic. Therefore, a change in bulk deposition of metals from the atmosphere need not be hypothesized to explain these results.

Third, in Nelson Lake, most of the input of each metal was retained in the lake. The retention varied from 68% (Ni) to 91% (Zn).

Fourth, in Hannah and Middle Lakes, both of which had been treated with neutralizing agents prior to the mass balance measurements, there was retention of Cu, Fe, Al and Zn. There was some retention of Cu, Fe, al and Zn. There was some retention of Mn in Hannah Lake, but none in Middle Lake, while more Ni left each lake via outflow than entered. Because these results for Ni were surprising, the mass balances were recalculated for Middle and Hannah Lakes using exports measured for Middle Lake watershed 1, instead of Clearwater Lake watershed 1, to estimate the contribution from the ungauged areas of each lake's watershed. Although there were much less data collected for the Middle lake watershed, these results may be more realistic, since the bulk deposition of metals at Sudbury Center (Middle and Hannah Lakes) was greater than at Sudbury South (Clearwater and Lohi Lakes, see Chapter 2). In all cases except Fe, these recalculated inputs were higher than the first estimates. As for Nelson Lake, all metals were partially retained in Middle and Hannah Lakes; that is, the input was greater than the output. Thus, in all 3 of the lakes that were not acidified at the time of the mass balance measurements, significant amounts of the metals were retained.

The retention of metals in the study lakes during the subsequent 12-month period (June 1978-May 1979), which included the periods when the smelters were shut down, was very different from the first 12-month period (Tables A10-96 to A10-100). The proportions of the metal inputs retained were always higher in the period after the shutdown. However, comparison of the mass balances for the 2 time periods indicates that the apparent increased retention was a result of reduction in the inputs, not an increase in outputs. This is expected, since the residence times of the lakes are much greater than the length of the shutdown period; therefore, reduced atmospheric deposition during shutdown (Chapter 2) cannot be expected to be reflected in the losses from the lakes via outflow. These results, as indicated in section C, demonstrate that the inputs were reduced during shutdown.

Since most of the metals behaved like conservative substances in the acidic lakes, their predicted concentrations (equation 8-3) should be comparable to those measured. As expected (Table 8-44), predicted and measured Cu and Ni concentrations were almost identical in both acidic lakes. Zinc and Mn concentrations in Lohi Lake were accurately predicted, as was the Al concentration of Clearwater Lake, while the measured Fe concentration was, as expected, much less than predicted in both lakes.

Because the steady-state concentration of a conservative substance is proportional to its input rate, reductions in input required to achieve specified concentrations are easily calculated. If the Great Lakes Water Quality Objectives (International Joint Commission 1976) are used as guidelines (Cu - 5 $\mu g\ L^{-1}$, Ni -

Table 8-44. Predicted and measured concentrations of metals in Clearwater and Lohi Lakes. Predicted values are based on mass balances for 1977-1978. All figures in μg L^{-1}.

	Clearwater Lake[1]		Lohi Lake	
	predicted	measured[1]	predicted	measured[2]
Cu	80.3	86.4	74.8	83.6
Ni	269	274	224	254
Zn	65.0	47.0	40.3	41.6
Fe	811	91.2	236	90
Mn	183	296	283	284
Al	421	389	302	–[3]

[1] average values for 1976-77

[2] average values for 1973 at 1 m above bottom

[3] no data

25 µg L^{-1}, Zn - 30 µg L^{-1}, Fe - 300 µg L^{-1}, no criteria for Mn or Al), then the reductions in inputs required to achieve these concentrations in Clearwater and Lohi Lakes are (based on the concentrations predicted by the mass balance model) ~95%, 90%, 55% and 65% for Cu, Ni, Zn and Fe, respectively.

Although no criteria are yet available for Mn, a concentration of 100 µg Al L^{-1} has been suggested as a level that will not cause damage to fish populations (Ontario Ministry of the Environment 1978). The observed levels in the study lakes have been shown to result in mortalities in brook trout and white sucker populations in soft, acidic (pH 4.4 - 5.2) water (Driscoll et al. 1980). Approximately 76 and 67% reductions in input of Al to Clearwater and Lohi Lakes, respectively, are required to achieve a reduction to 100 µg L^{-1}.

For Middle and Hannah Lakes, mass balances were calculated using Middle Lake watershed 1 data to estimate contributions from the ungauged portions of the watersheds. Preliminary calculations using Clearwater Lake watershed 1 data resulted in predictions of Ni concentrations (Table 8-45) that were substantially lower than those measured. Since this implies that the concentration was not at steady-state (contradicting the observed findings, see Appendix 10) or that an internal source of Ni supplied input (contradicting the fact that Ni was accumulating in the lakes' sediments, see Chapter 3), it was apparent that inputs estimated on the basis of Clearwater Lake watershed 1 were too low.

In Middle and Hannah Lakes, the measured concentrations were always lower than the predicted concentrations. This retention or removal of the metals in Middle and Hannah Lakes is, of course, expected because of their pH. Comparison of predicted steady-state

Table 8-45. Predicted and measured metal concentrations in Hannah and Middle Lakes. Predicted values are based on mass balances for 1977-1978. All figures in $\mu g\ L^{-1}$

	Hannah Lake				Middle Lake			
	predicted[1]		measured[2]		predicted[1]		measured[3]	
Cu	231	(402)	46.7	(1110)	179	(320)	63.7	(496)
Ni	276	(807)	410	(1870)	401	(838)	445	(1060)
Zn	52.9	(76.1)	27.7	(120)	43.9	(62.6)	35.4	(91.3)
Fe	800	(581)	120	(47.0)	644	(464)	140	(143)
Mn	168	(195)	135	(340)	189	(210)	228	(354)
Al	314	(533)	65.0	(1100)	323	(504)	65.6	(-)

[1] predicted values in brackets based on mass balances calculated using Middle Lake watershed 1 data instead of Clearwater Lake watershed 1 data for estimation of the contribution from the ungauged area

[2] average values for 1976-1977; values in brackets are for 1 m below surface in 1974 prior to neutralization

[3] average values for 1976-1977; values in brackets are for 1 m above bottom in 1973 prior to neutralization

concentrations based on 1977-1978 data with concentrations measured in the lakes prior to neutralization treatments (1974 data for Hannah Lake, 1973 data for Middle Lake) indicate (Table 8-45) that the earlier levels of Cu, Ni, Zn, Mn and Al were in excess of concentrations that could be supported by current inputs, even if none of the metals were lost by sedimentation.

Results obtained for Nelson Lake are reported in Table 8-46. The measured concentrations of Cu, Ni, Zn, Fe, Mn and Al in 1977 were all substantially lower than those predicted using the conservative substance mass balance model. However, the predicted Cu, Ni and Mn concentrations were comparable to those measured in 1975, prior to neutralization, even though the pH of the lake was ~5.6. Most of the Fe and some of the Al and Zn were apparently retained in the lake and deposited in the sediments. These results indicate that the Cu, Ni and Mn were behaving like conservative substances at a pH that was considerably higher than that measured in Clearwater and Lohi Lakes.

It is more difficult to estimate the reduction in inputs of metals required to lower the concentrations of Middle, Hannah and Nelson Lakes to acceptable levels. Calculations can be based on either measured or predicted lake concentrations. In the former case, the lake's ability to remove the metals from the water column to the sediments is taken into account; however, this capability may change in an unknown manner with changes in input rates. The simplest assumption is that a constant fraction of the input is removed from the water column. If this is true, then reductions in input of 89 and 94% are required for Cu and Ni, respectively, for Hannah Lake, while Fe and Zn are already at acceptable levels. On the other hand, if the required reductions are based on the

Table 8-45. Predicted and measured metal concentrations in Nelson Lake. Predicted values are based on mass balances for 1977-1978. All figures in μg L^{-1}.

	predicted	measured	
		1977	1975[1]
Cu	25.7	3.9	22.0
Ni	17.1	6.9	17.1
Zn	38.6	5.7	18.3
Fe	233	19.2	60.8
Mn	57.2	13.2	63.1
Al	181	21.1	86.6

[1] pre-neutralization data only

concentrations using the conservative substance steady-state model, then the lakes' ability to effectively remove the metals from the water column is ignored. However, there are 2 reasons to use this approach. Although the removed metal does not remain in the water column, it is stored in the lake sediments. It may, therefore, affect the benthic organisms. Second, the steady-state lake concentration of a conservative substance is equal to the mean volume-weighted inflow concentration. Therefore, to be sure to attain acceptable metal concentrations for biota living in the streams as well as the lake, this latter calculation is preferred. Under these circumstances, very large reductions in Cu (99 and 98% for Hannah and Middle Lakes, respectively), Ni (97 and 97% for Hannah and Middle Lakes, respectively), Zn (61 and 52%, respectively), and Fe (48 and 35%, respectively), are required. To achieve Al levels of only 100 μeg L^{-1}, reductions in input of 68 and 69% are required for Hannah and Middle Lakes, respectively. For Nelson Lake, reductions in only Cu (81%) and Zn (22%) are necessary.

In summary, reductions in Cu and Ni inputs of at least 90% , and possibly as high as 99%, are required to attain suitable concentrations in the study lakes. Reductions in Zn and Fe of 50 - 65 are also required to attain suitable concentrations in the lakes within at least 10 km of Copper Cliff. Reductions of 67 - 76% in Al input are also required for these lakes.

M. Summary

1. The concentrations of Mg^{2+}, K^+ and Na^+ in Clearwater and Lohi Lakes and Mg^{2+}, K^+, Na^+ and Cl^- in Nelson Lake were at steady state and were predictable using a simple mass balance model. Mg^{2+} and K^+ concentrations appeared to be at steady state in Hannah and Middle Lakes but predicted concentrations

were much lower than measured concentrations, indicating that the inputs had been underestimated.

2. The Cl^- concentrations in Clearwater, Lohi, Middle and Hannah Lakes increased over the duration of the study as a result of treatment of roads in the lakes' watersheds with $CaCl_2$ and/or NaCl. Road applications were responsible for 95 to 98% of the total input of Cl^- to Middle and Hannah Lakes. The Ca^{2+} inputs associated with application of $CaCl_2$ were calculated from the Cl^- inputs not associated with Na^+.
3. Except for the third treatment in Lohi Lake, Ca^{2+} levels increased after neutralization by an amount expected on the basis of complete dissolution of added $CaCO_3$ and/or $Ca(OH)_2$. After corrections for extra inputs of Ca^{2+} associated with $CaCl_2$, levels in Clearwater and Lohi Lakes subsequently declined according to a simple washout model. Concentration of Ca^{2+} in Hannah and Middle Lakes was greater than predicted; hence, Ca^{2+} inputs used to make the prediction must have been underestimates.
4. The measured input of mineral acidity to Clearwater lake in 1977-78 was sufficient to maintain the lake's alkalinity at ~-50 μeq L^{-1} (pH ~4.3), very near the measured concentration. The pH of the lake will not increase unless this acidity input is reduced.
5. Predictions based on the mass balance model indicated that Lohi Lake would re-acidify (ie. have no remaining acid neutralizing capacity or ANC) in late 1976. Re-acidification occurred only 6-9 months later. The alkalinity of the lake stabilized at ~-15 μeq L^{-1}, 20-30 μeq L^{-1} greater than predicted, indicating that there was an unmeasured internal generation of ANC or that the inputs of mineral acidity were overestimated.

6. The measured ANC in Middle and Hannah Lakes were always much greater than ANC predicted by the mass balance model. Residual ANC would have been exhausted in mid to late 1978 in Hannah Lake and in mid 1975 in Middle Lake according to the model. InHannah Lake, measured ANC was in fact higher in late 1978 than immediately after neutralization. ANC supplied by NO_3^- uptake by the biota following fertilization could account for only 4-12% and 11-46% of the extra ANC generated in Hannah and Middle Lakes respectively. It was hypothesized that the remainder of the ANC was released from the sediments which had been previously neutralized by the additions of $CaCO_3/Ca(OH)_2$.
7. The measured inputs of SO_4^{2-} to Clearwater and Lohi Lakes could not account for the observed concentrations in the lakes. An additional input of SO_2 to the lakes' surfaces that was not measured in the bulk deposition collectors was the source of the extra SO_4^{2-}. The bulk deposition measurements accounted for only 33% of the total input of SO_4^{2-} and SO_4^{2-} producing substances to the whose watersheds (40% to the terrestrial portion and 24% to the lake surfaces). Similarly, unmeasured SO_2 inputs to Middle and Hannah Lakes accounted for 66 to 80% of the total.
8. The concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) in Hannah and Middle Lakes are much greater than predicted using the measured or estimated mass balances and steady-state model. Calculation of the inputs from the watersheds required to achieve the observed lakes concentrations allowed estimation of the input of strong acids to the watersheds. This calculated input was much greater than the measured bulk deposition of

strong acids by an amount almost identical to the "additional" SO_4^{2-} predicted by the SO_4^{2-} mass balances.

9. Comparison of 4 different methods of calculating the excess acid deposition demonstrated that;

   a) all results were in good agreement

   b) the unmeasured acid input was H_2SO_4 derived from oxidation of dry deposited SO_2, and

   c) this component of the acid input was larger than all other measured components being ~70%, ~80 to 90%, and ~67% of the total input for the Middle, Hannah and Clearwater-Lohi Lake watersheds respectively.

10. In the acidic lakes (Clearwater and Lohi), Cu, Ni and Al behave as conservative substances; that is, they are not lost to the lakes' sediments. This is the most probable explanation for the observation (Chapter 3) that their concentrations in sediments deposited in the last 1-3 decades are lower than those in older sediments. Their concentrations were accurately predicted by the same mass balance model that was used for major ions. Reductions in inputs required to meet accepted standard concentrations are 95% for Cu, 90% for Ni, 55% for Zn, 65% for Fe and ~ 70% for Al. These proposed reductions do not take into account the beneficial effects on metal concentrations that would result if the lake pH was concurrently increased. On the other hand, the acceptable concentrations may be too great because they were proposed for hard-water lakes. In the non-acidic lakes (Hannah, Middle and Nelson), much of the input of Cu, Ni, Zn, Al and Fe was retained in the lakes' sediments. Estimated reductions in input needed to meet accepted criteria are as high as 99% for Cu, 97% for Ni, 61% for Zn, 48% for Fe and 69% for Al.

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Fig. 8-1. Measured (solid circles) and predicted Ca^{2+} concentration in Clearwater Lake. Predictions based on annual mass balances (——) and monthly mass balances (- - - -) are shown.

Fig. 8-2. Measured (solid circles) and predicted Ca^{2+} concentration in Clearwater Lake. Predictions were made with the initial value for June 1973 set at 6.0 mg L^{-1} (as in Fig. 8-1) and at 5.5 mg L^{-1}.

Fig. 8-3. Measured (solid circles) and predicted Ca^{2+} concentration in Lohi Lake. The upper pair of lines after June 1975 represent an increase in Ca^{2+} concentration resulting from the third neutralization treatment only (–▲–▲–), or the neutralization treatment + $CaCl_2$ additions resulting from road applications (——). The lower pair of lines again represent neutralization (–▲–▲–) and neutralization plus $CaCl_2$, but with the neutralization treatment supplying 2.2 mg L^{-1} instead of 3.25 mg L^{-1} of Ca^{2+}.

Fig. 8-4. Measured (solid circles) and predicted Ca^{2+} concentration in Lohi Lake based on a third neutralization treatment (June 1975) providing 3.25 mg Ca^{2+} L^{-1} and additions to the lake resulting from road applications of $CaCl_2$. Predictions based on annual mass balances (——) and monthly mass balances (- - - -) are shown.

Fig. 8-5 . Measured (solid circles) and predicted Ca^{2+} concentration in Hannah Lake. The neutralization

treatment in June 1975 resulted in an instantaneous increase in Ca^{2+} concentration. The upper line includes additions from $CaCl_2$ applications. From June 1977 - December 1979, predictions were based on long-term steady-state Ca^{2+} budgets including (-x—x-) and excluding (-■-■-) $CaCl_2$ inputs, and measured Ca budgets including (——) and excluding (-▲-▲-) $CaCl_2$ inputs.

Fig. 8-6. Measured (solid circles) and predicted Ca^{2+} concentration in Middle Lake. Results are shown, beginning in June 1975, with and without $CaCl_2$ inputs. Predictions from June 1977 to December 1979 were based on long-term steady-state Ca^{2+} budgets including (-x—x-) and excluding (-▲-▲-) $CaCl_2$ inputs, and measured Ca^{2+} budgets including (——) and excluding (-■-■-) $CaCl_2$ inputs.

Fig. 8-7. Measured (solid circles) and predicted Ca^{2+} concentration in Nelson Lake. Predictions from June 1977 to December 1979 were based on annual mass balances (——) and monthly mass balances (----). Nelson Lake was treated with $CaCO_3$ and $Ca(OH)_2$ in 1975 and 1976.

Fig. 8-8. Aqueous carbonate equilibrium at constant pCO_2 (from Stumm and Morgan 1970).

Fig. 8-9. Alkalinity and acidity titrations as measures of acid and base neutralizing capacities (from Stumm and Morgan 1970).

Fig. 8-10. Measured and predicted alkalinity in Clearwater Lake. Measured values were based on TIA titrations (x), pH measurements (▲), C_T, Acidity and Al measurements

(●). Predicted alkalinity was based on model ALK 1 (Table 8-23).

Fig. 8-11. Measured and predicted alkalinity in Clearwater Lake. Measured values were based on TIA titrations (x), pH measurements (▲) and C_T, Acidity and Al measurements (●). Predicted concentrations were based on models ALK 2 (———), ALK 3 (— — —) and ALK 4 (------) (Table 8-23).

Fig. 8-12. Measured and predicted alkalinity in Lohi Lake. Measured values were based on TIA titrations (x), pH measurements (▲), C_T, Acidity and Al measurements (●), and corrected TFA measurements (o). Predicted concentrations were based on ALK 2 (———), ALK 3 (— — —) and ALK 4 (------) (Table 8-24).

Fig. 8-13. Measured and predicted alkalinity in Hannah Lake. Measured values were based on TIA titrations (x), pH measurements (▲), C_T, Acidity and Al measurements (●), and corrected TFA measurements (o). Predicted concentrations were based on ALK 2 (———), ALK 3 (— — —), and ALK 4 (------) (Table 8-25).

Fig. 8-14. Measured and predicted alkalinity in Middle Lake. Measured values were based on TIA titrations (x), pH measurements (▲), C_T, Acidity and Al measurements (●), and corrected TFA measurements (o). Predicted concentrations were based on ALK 2 (———), ALK 3 (— — —), and ALK 4 (------) (Table 8-26).

Fig.8-1

CLEARWATER LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

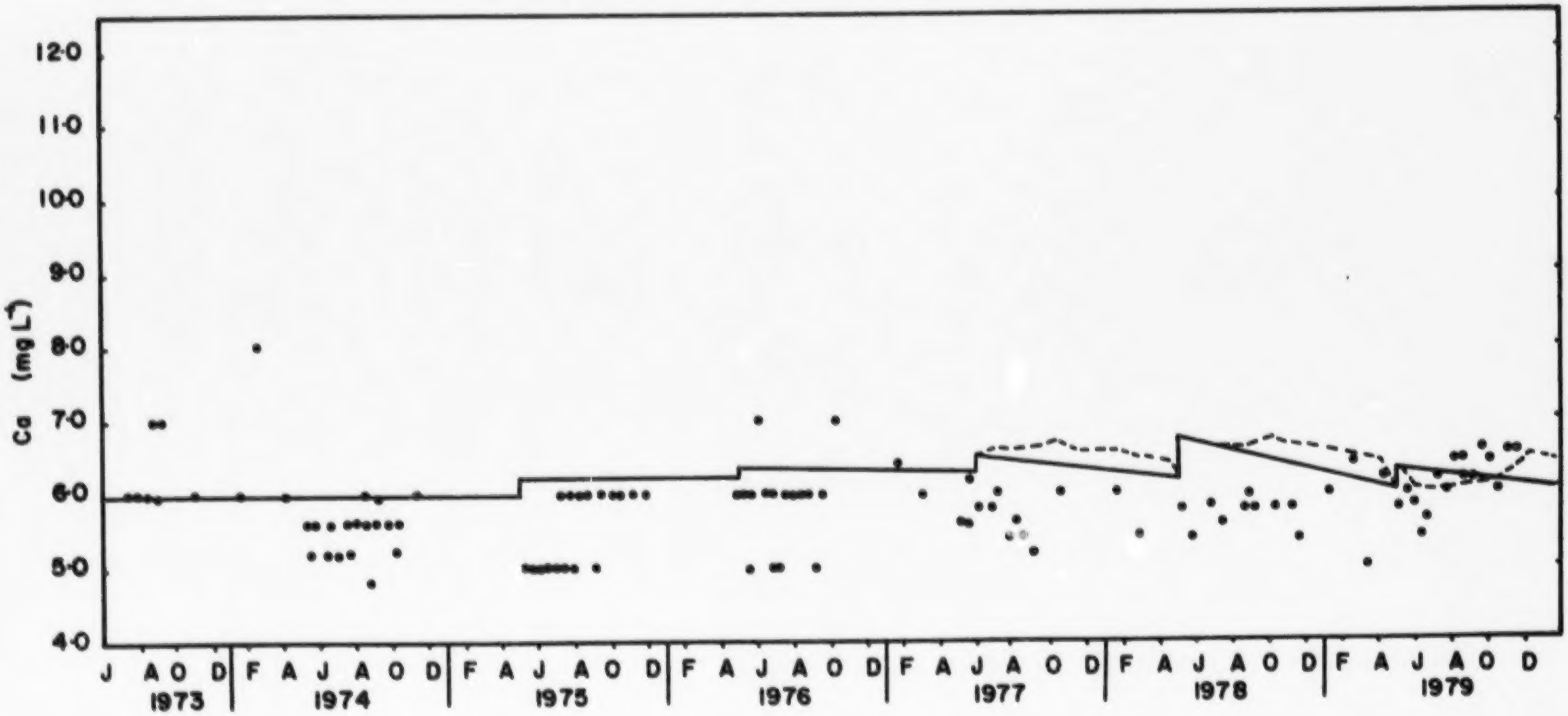


Fig.8-2

CLEARWATER LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

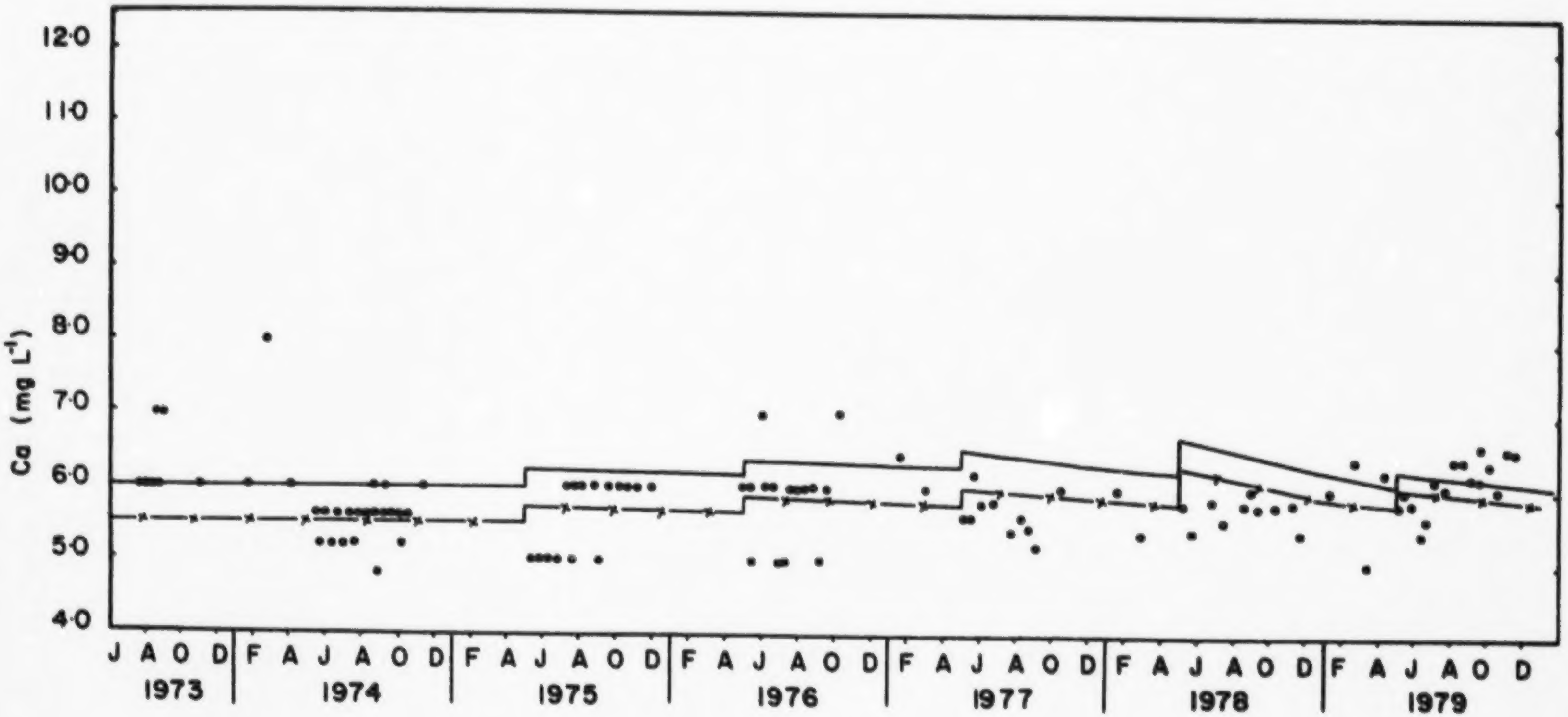


Fig.8-3

LOHI LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

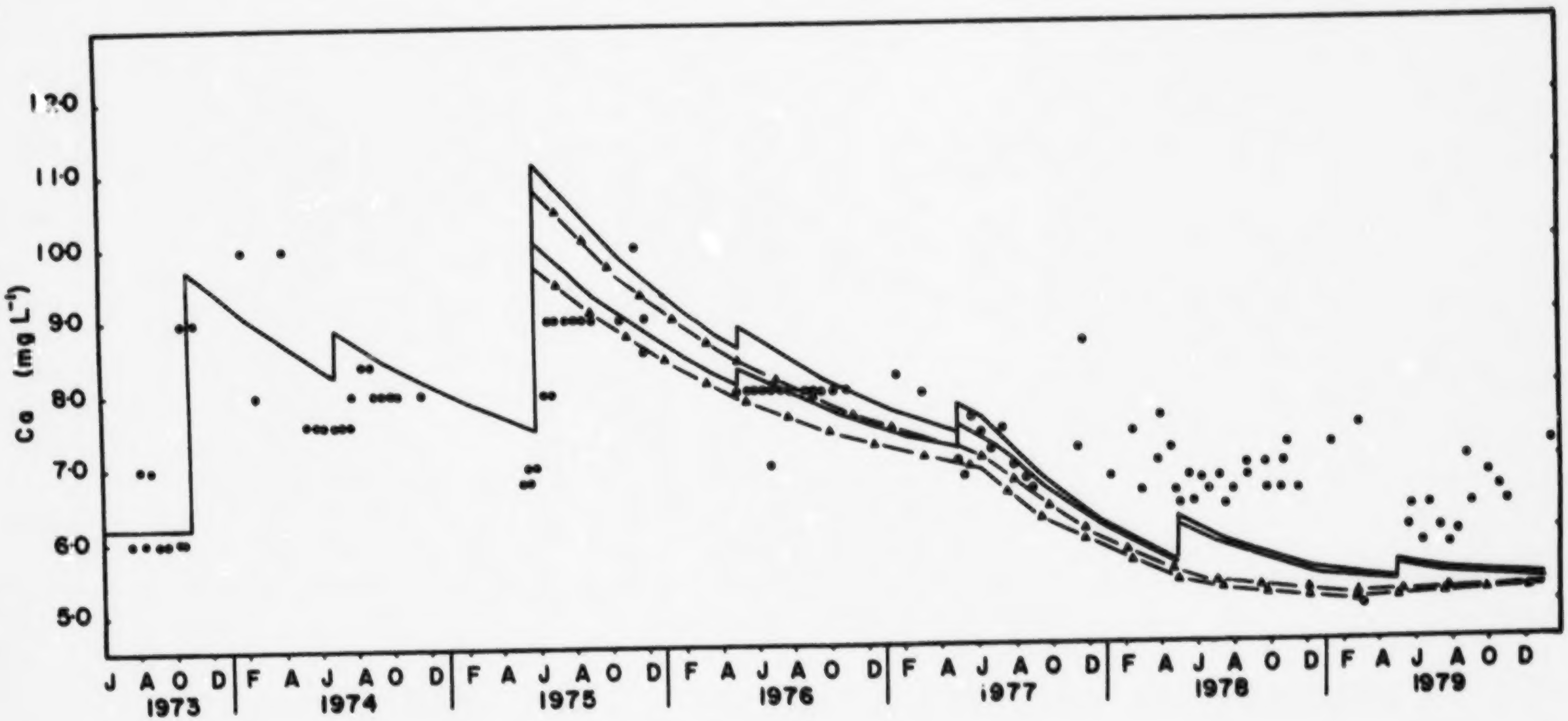


Fig.8-4

LOHI LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

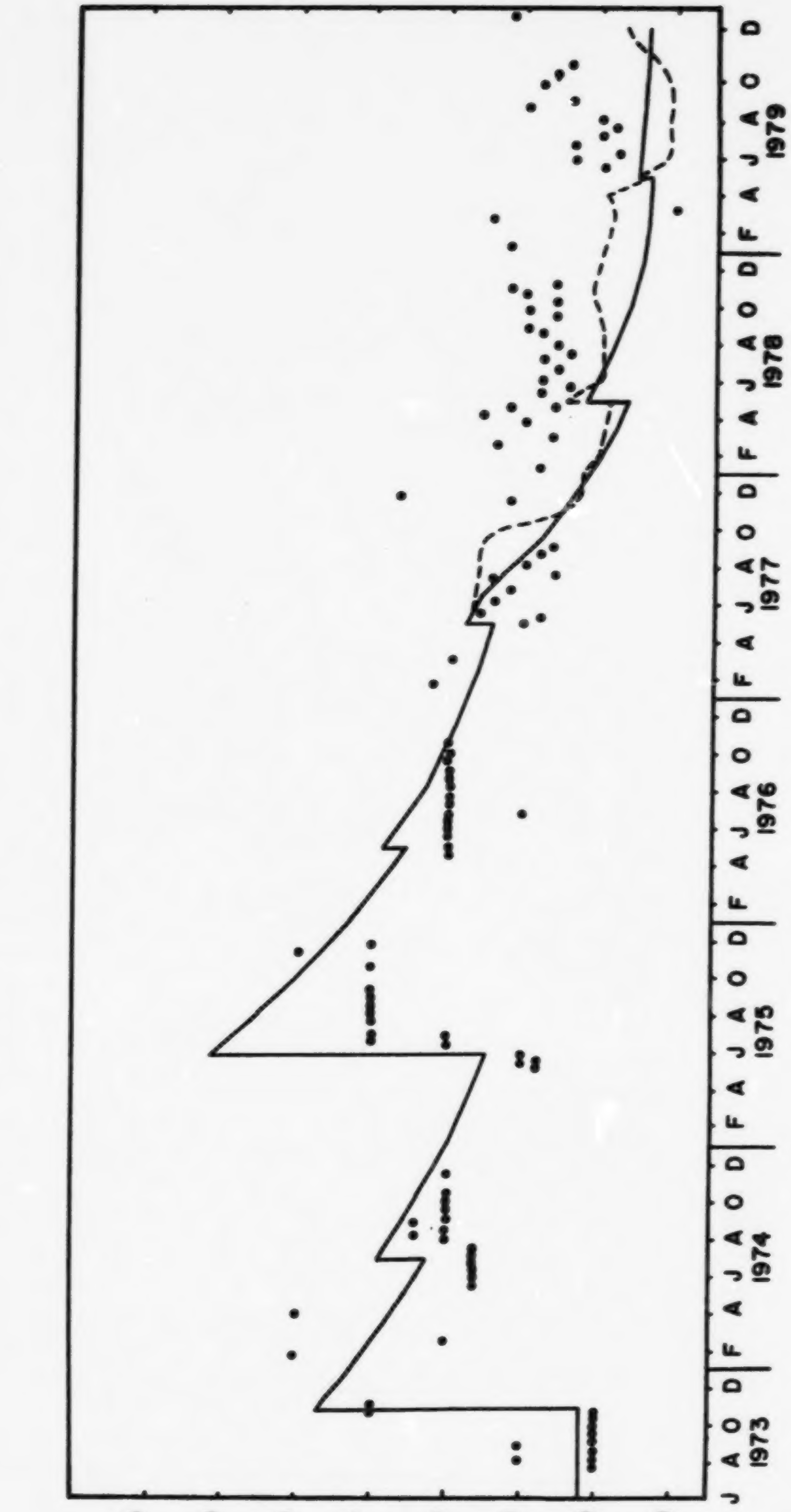


Fig.8-5

HANNAH LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

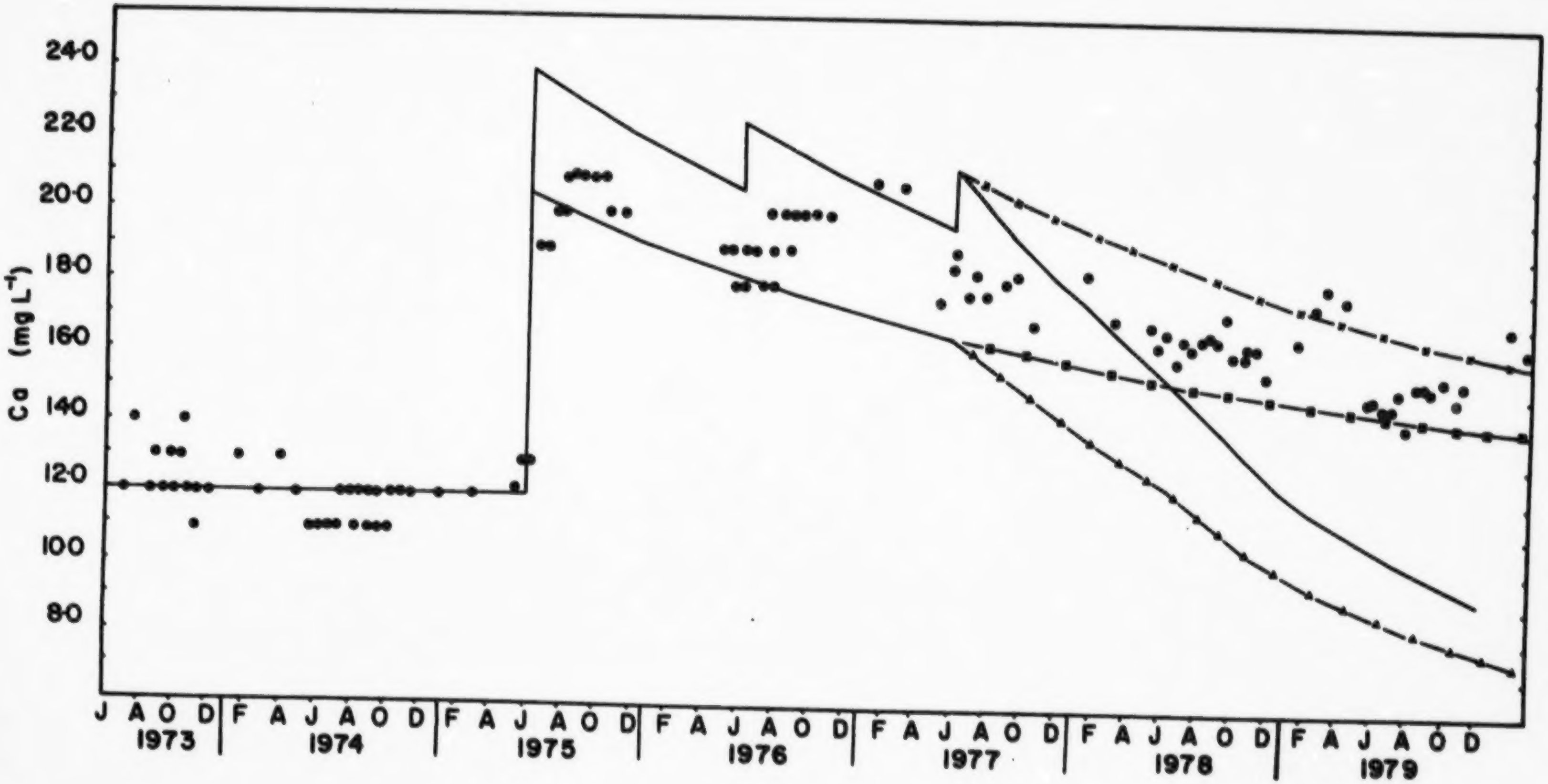


Fig.8-6

MIDDLE LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

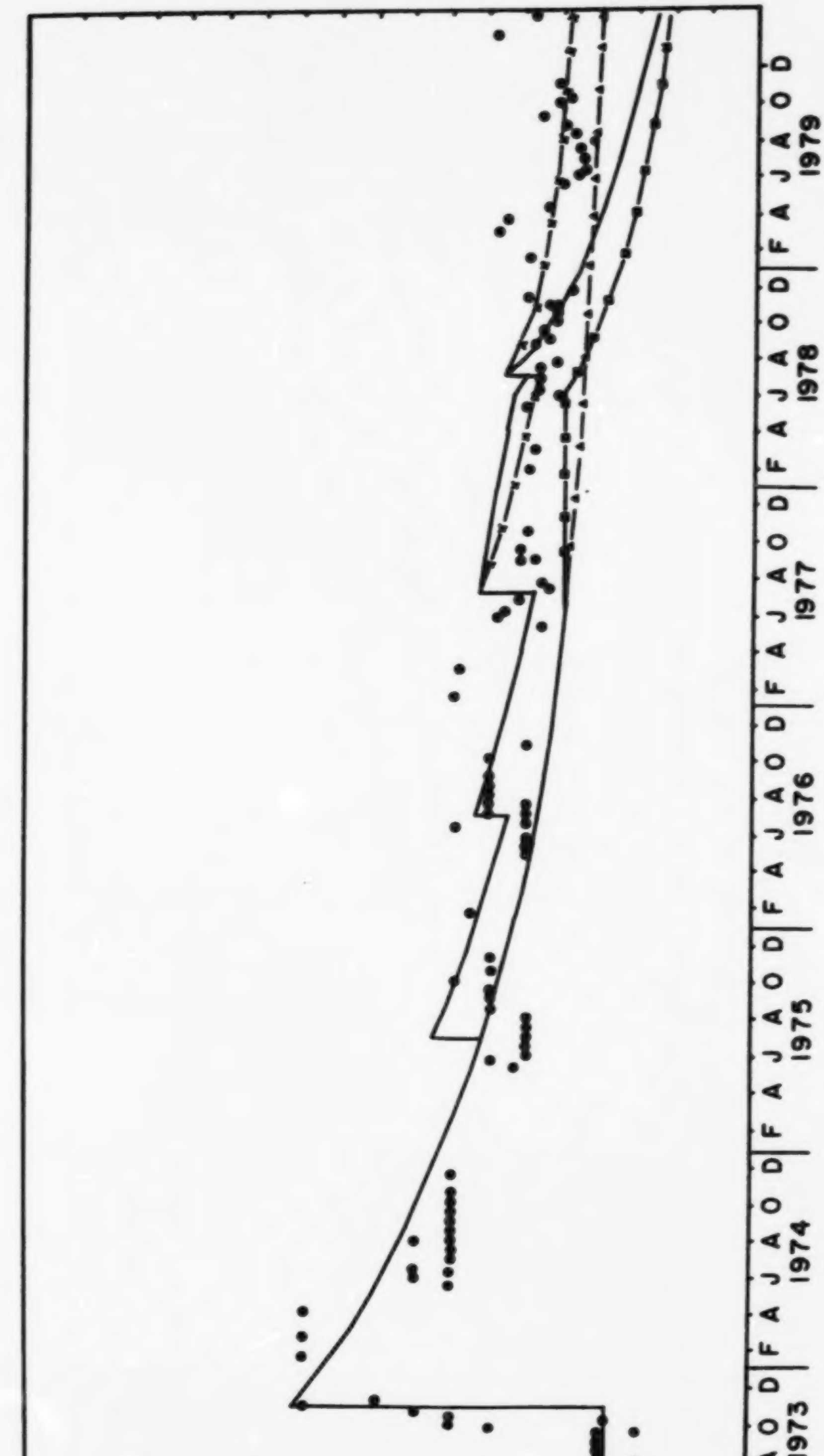


Fig.8-7

NELSON LAKE - Ca MODEL PREDICTIONS and MEASURED CONCENTRATIONS

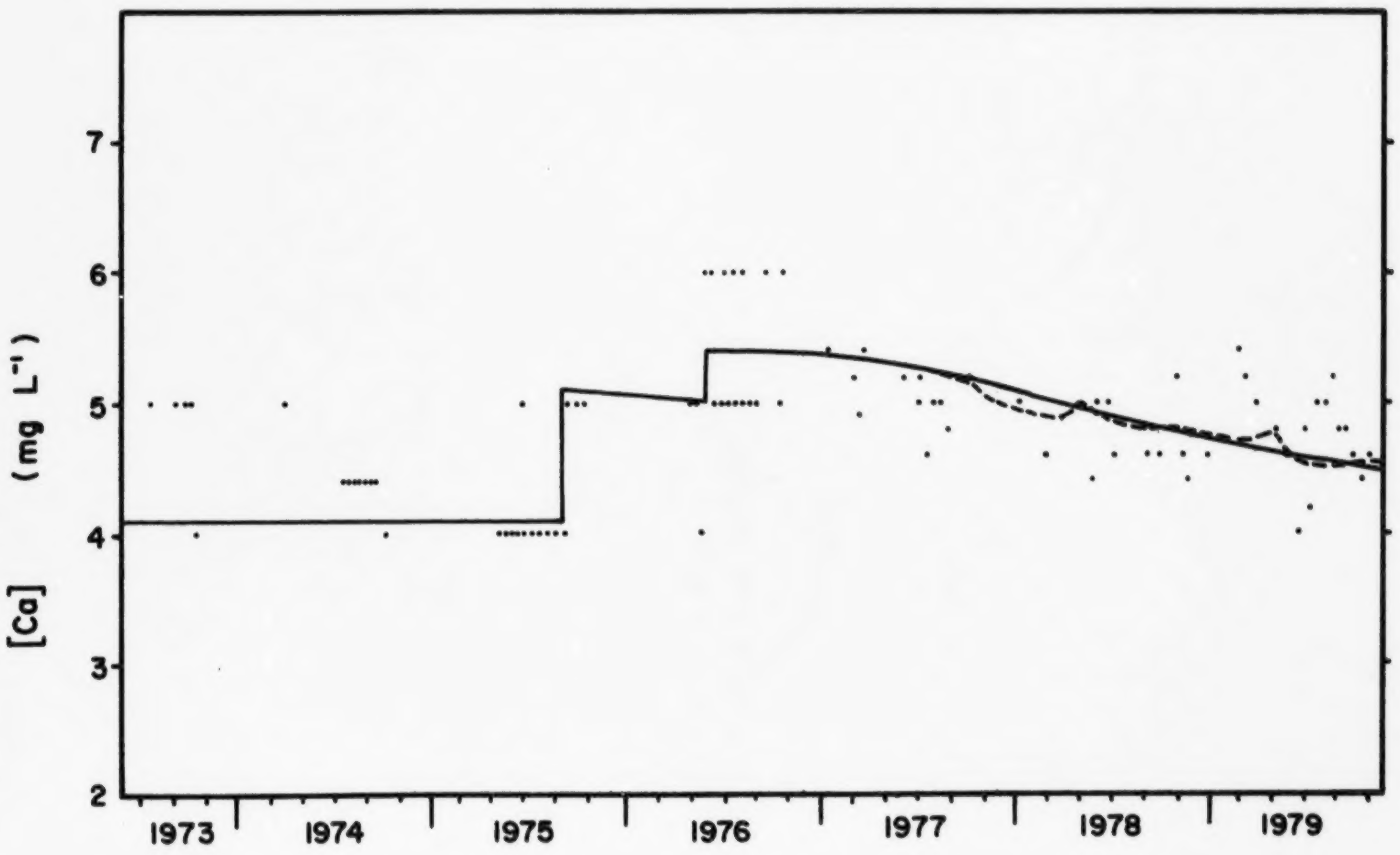


Fig.8-8

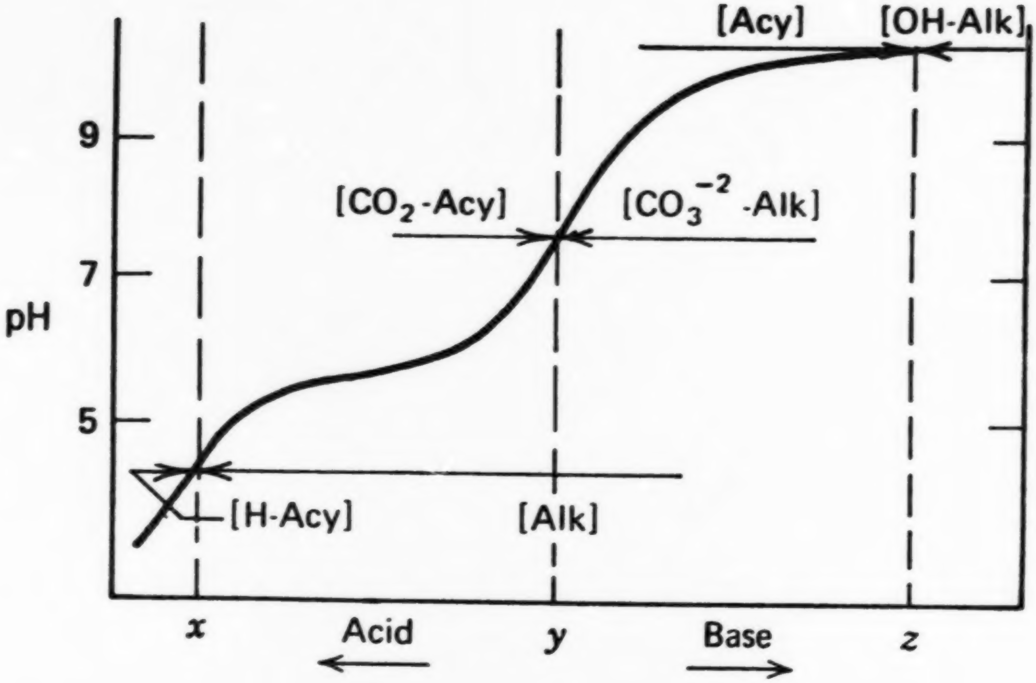


Fig.8-9

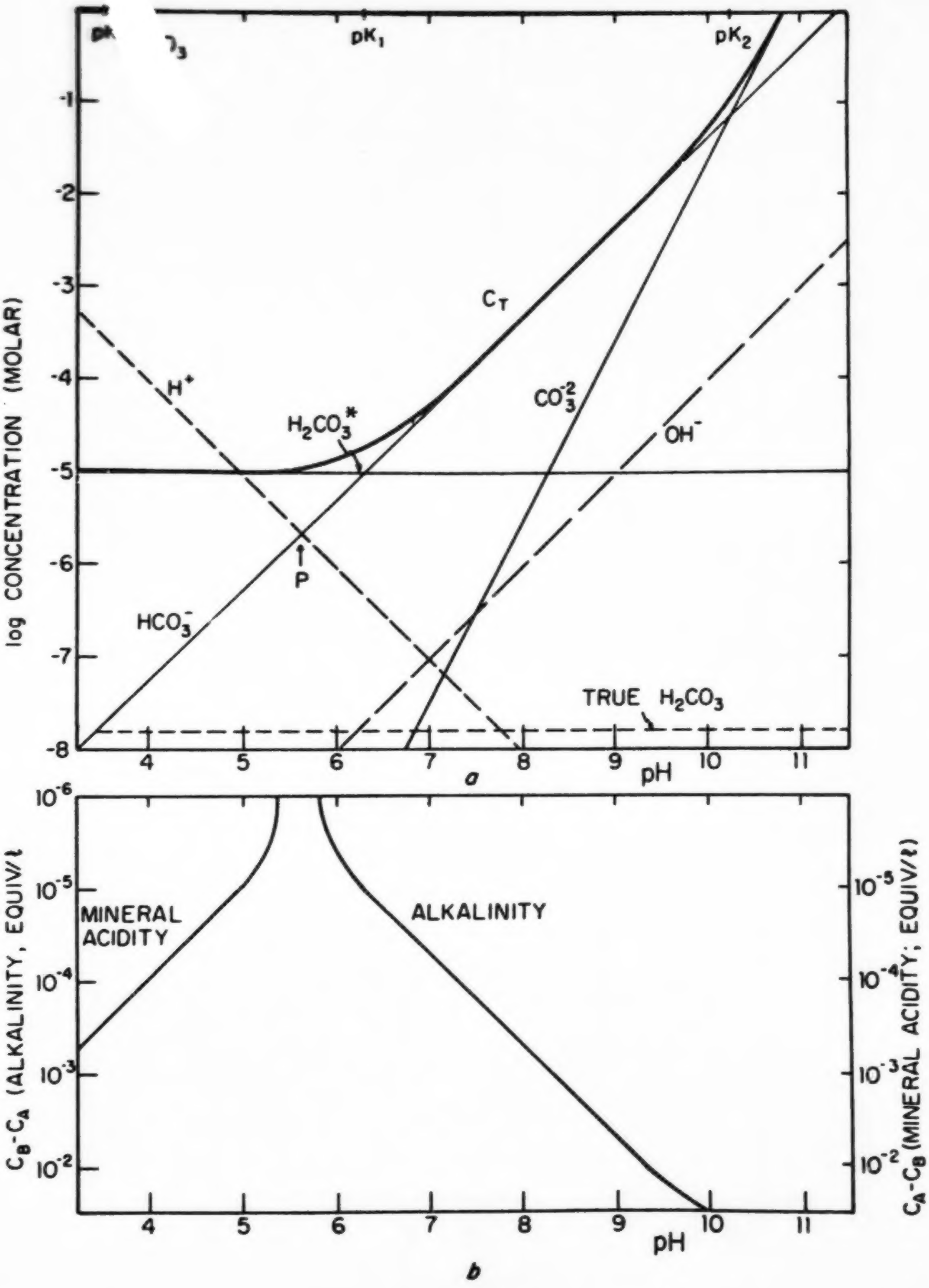

pK
pK$_1$
pK$_2$
log CONCENTRATION (MOLAR)
-1
-2
-3
-4
-5
-6
-7
-8
C_T
H^+
$H_2CO_3^*$
CO_3^{-2}
OH^-
P
HCO_3^-
TRUE H_2CO_3
4
5
6
7
8
9
10
11
pH
a
C_B-C_A (ALKALINITY, EQUIV/ℓ)
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
MINERAL ACIDITY
ALKALINITY
C_A-C_B (MINERAL ACIDITY; EQUIV/ℓ)
10^{-5}
10^{-4}
10^{-3}
10^{-2}
4
5
6
7
8
9
10
11
pH
b

Fig.8-10

CLEARWATER LAKE - ALKALINITY MODEL PREDICTIONS and MEASURED CONCENTRATIONS

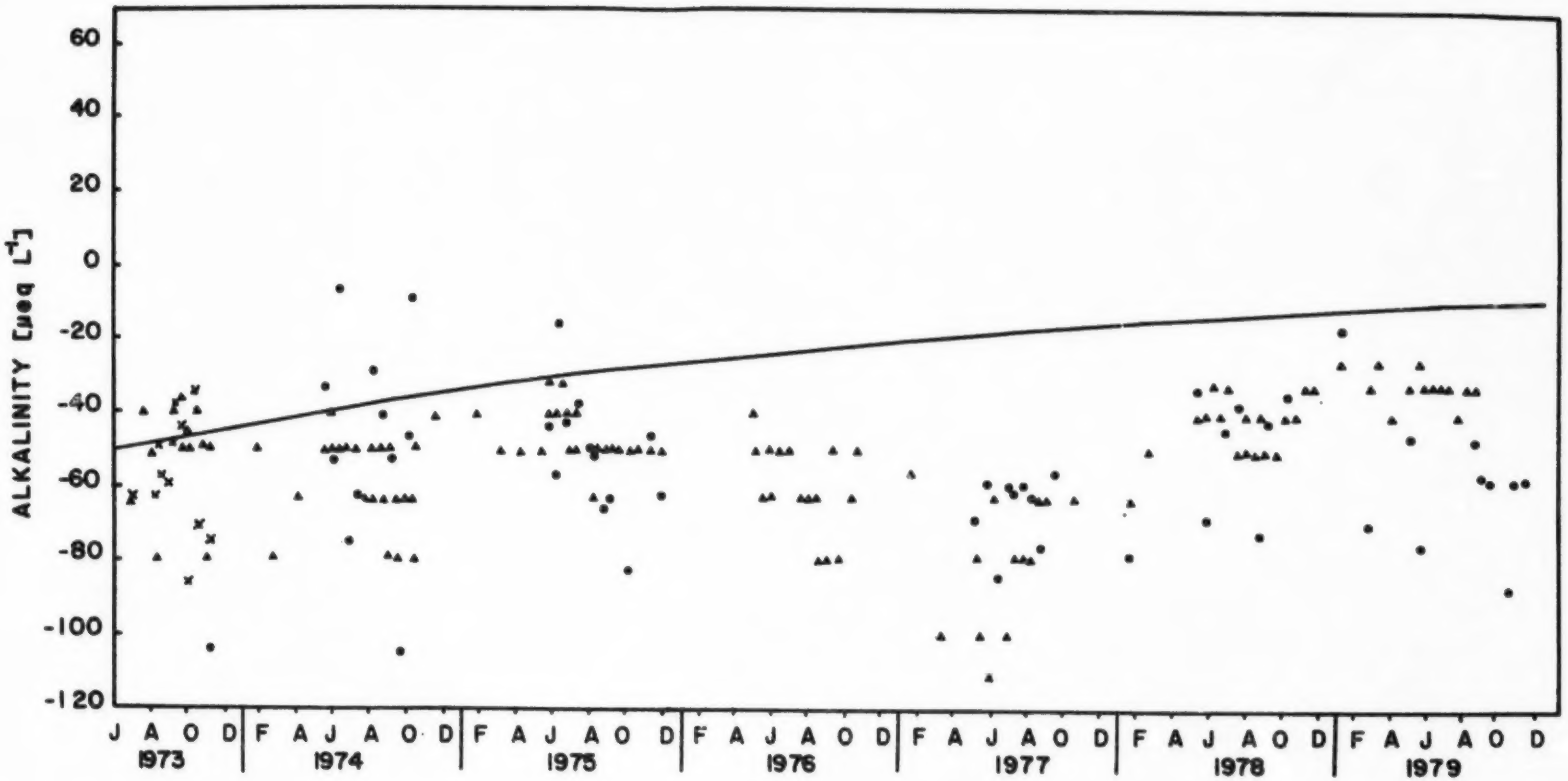


Fig. 8-11

CLEARWATER LAKE - ALKALINITY MODEL PREDICTIONS and MEASURED CONCENTRATIONS

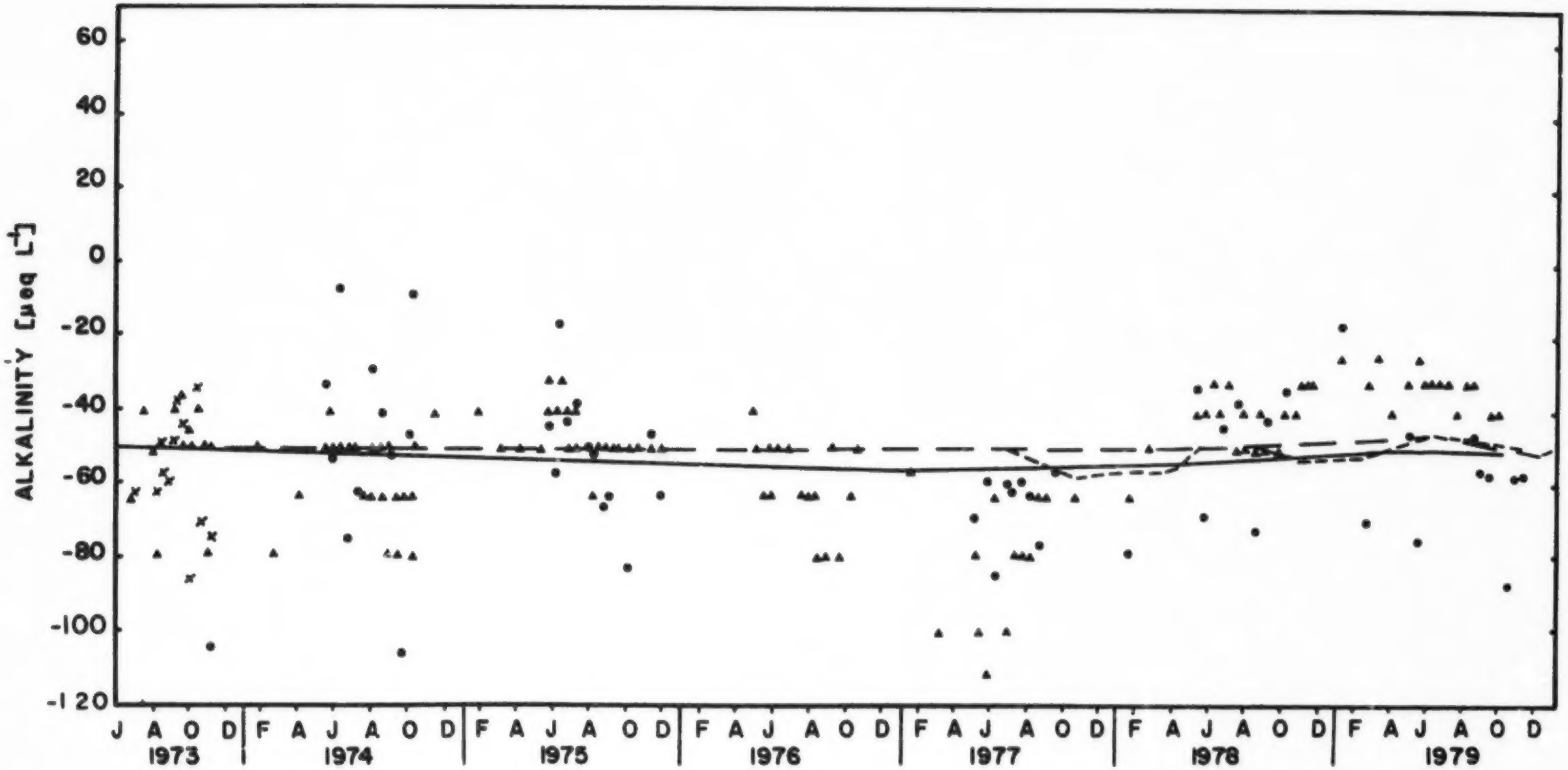


Fig.8-12

LOHI LAKE - ALKALINITY MODEL PREDICTIONS and MEASURED CONCENTRATIONS

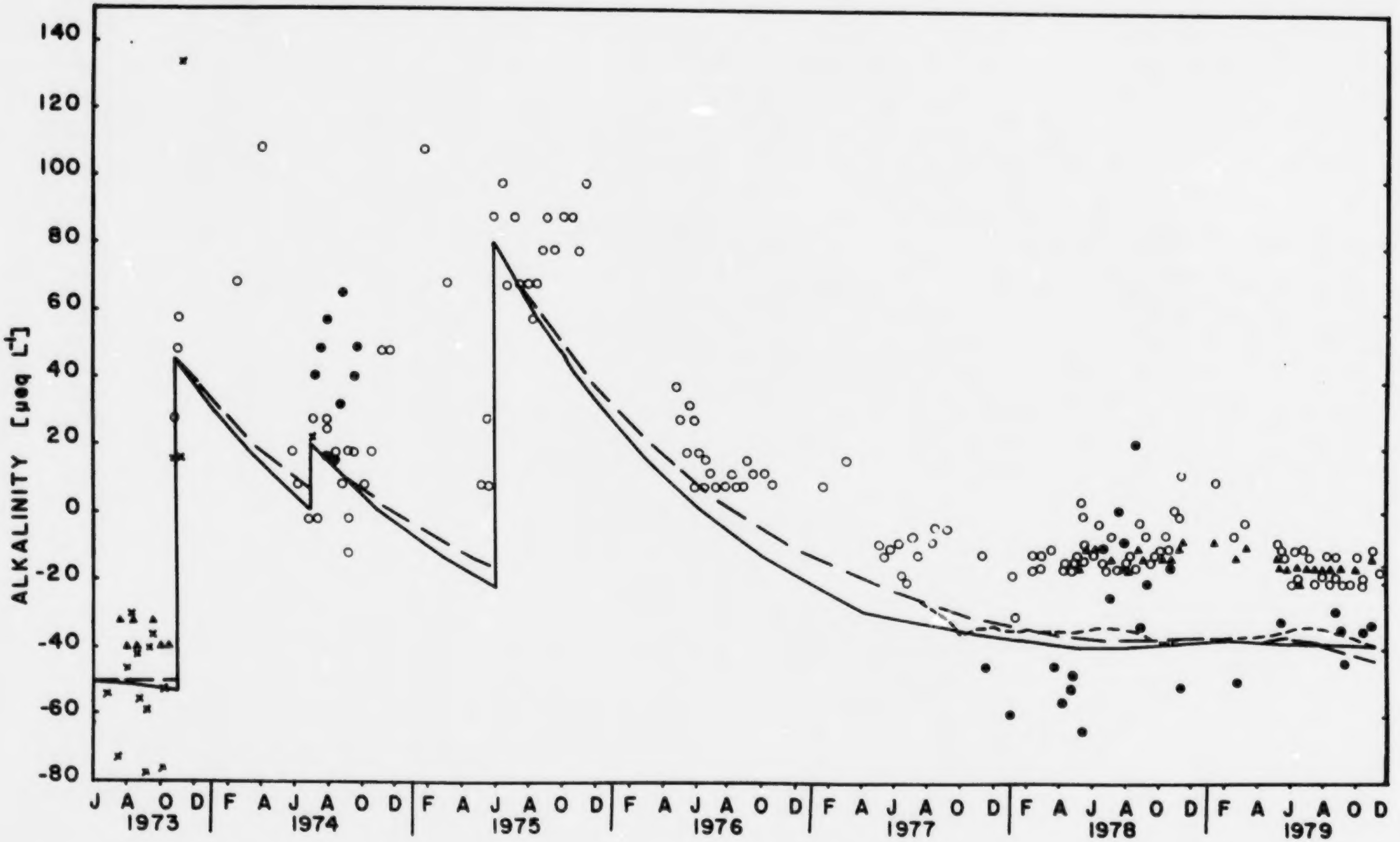


Fig.8-13

HANNAH LAKE - ALKALINITY MODEL PREDICTIONS and MEASURED CONCENTRATIONS

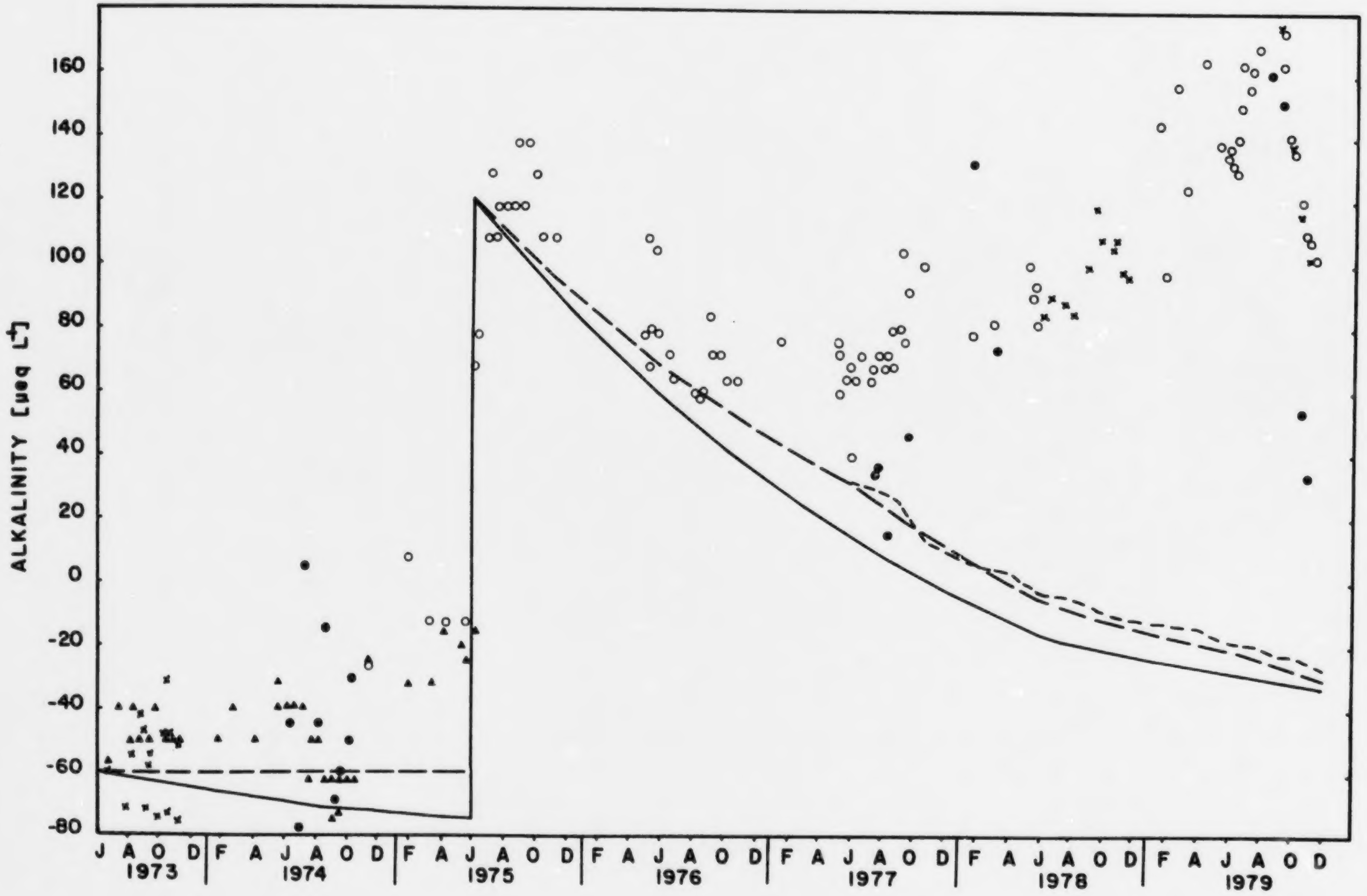
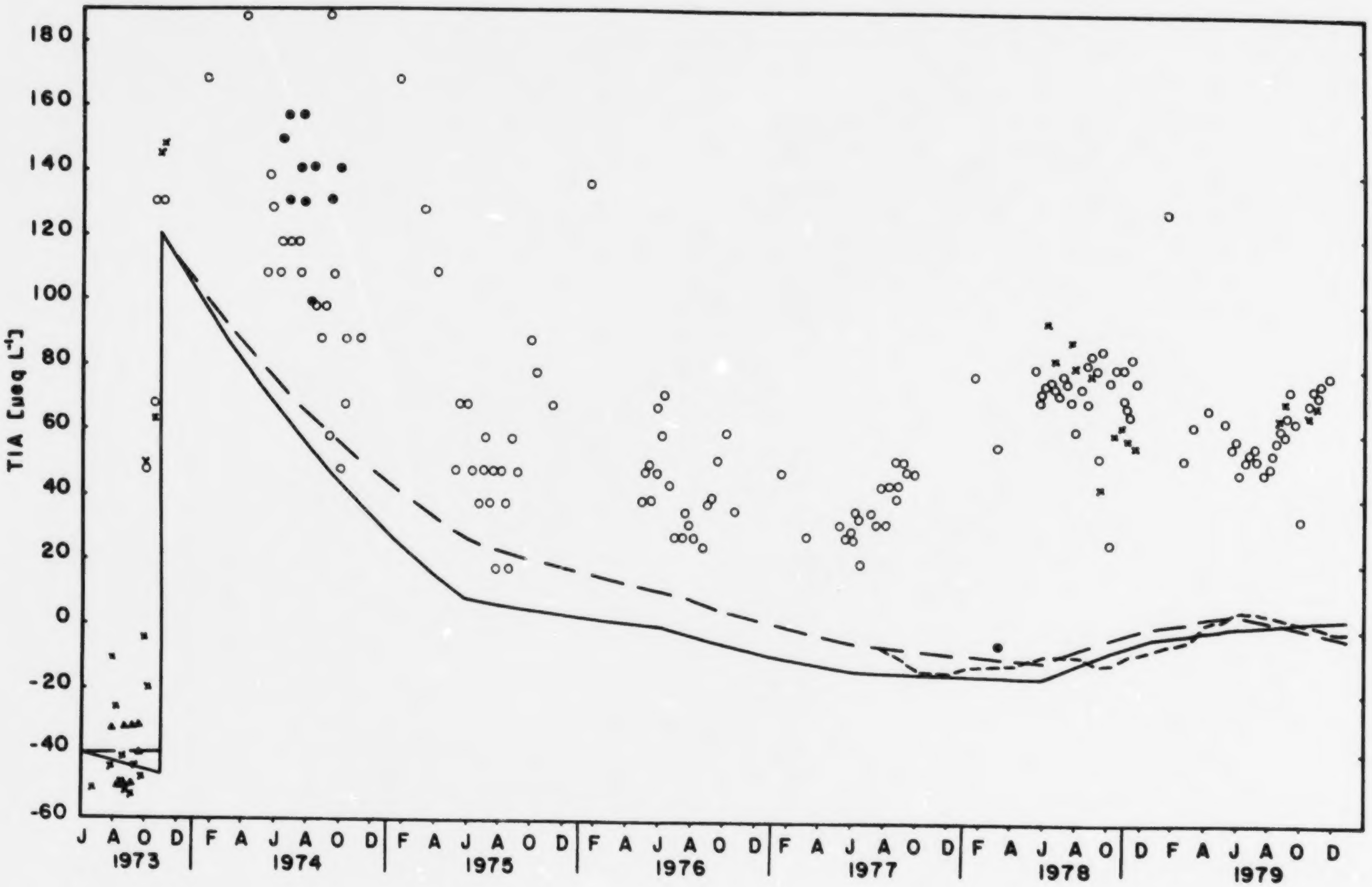


Fig.8-14

MIDDLE LAKE - ALKALINITY MODEL PREDICTIONS and MEASURED CONCENTRATIONS



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